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TESIS DOCTORAL

Desarrollo y evaluación de procesos de oxidación avanzada para el tratamiento de aguas residuales papeleras

Development and assesment of advanced oxidation processes for the treatment of pulp and paper mill effluents

MEMORIA PARA OPTAR AL GRADO DE DOCTOR

PRESENTADA POR

Noemí Merayo Cuevas

Directoras

Ángeles Blanco Suárez
María Daphne Hermosilla Redondo

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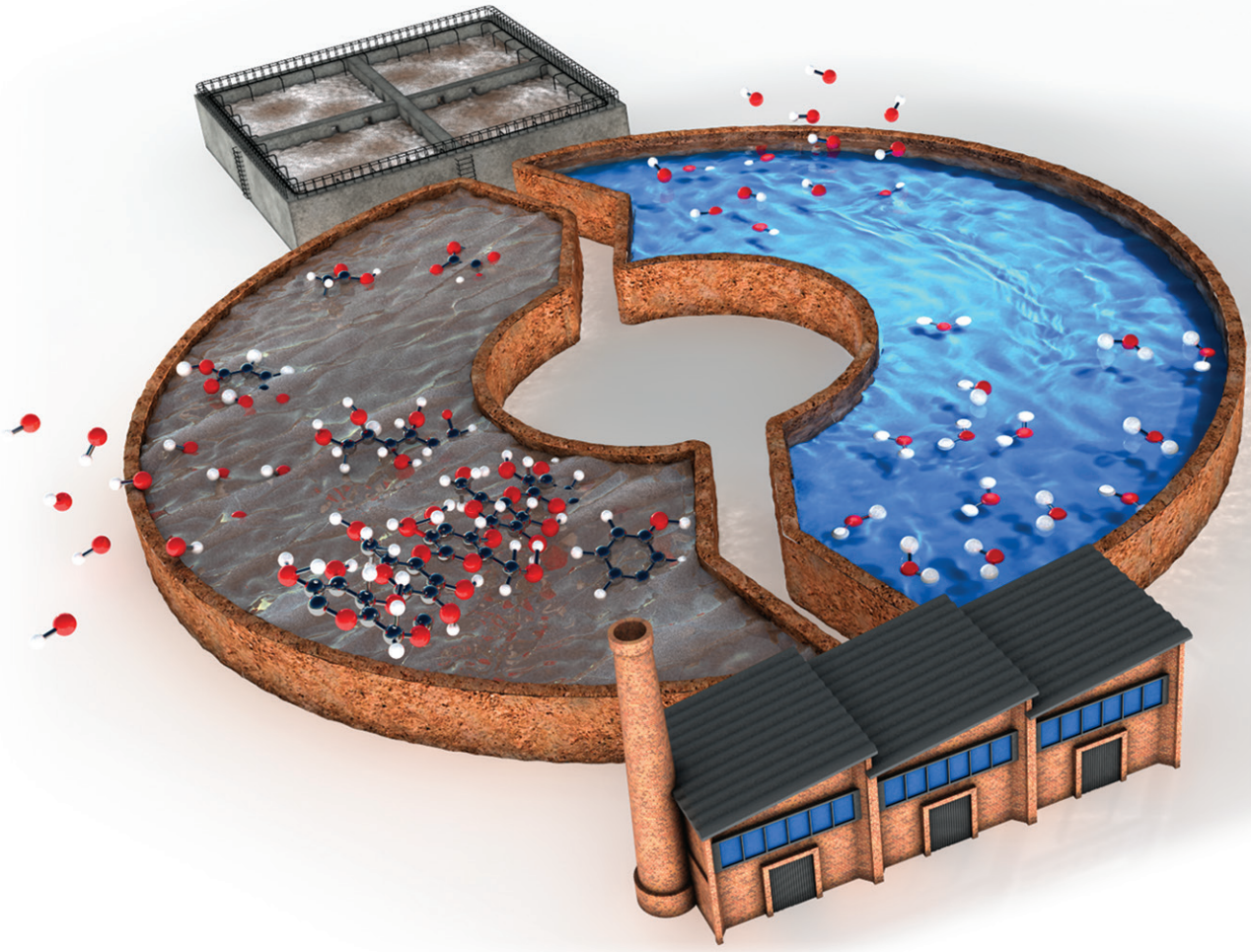

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Desarrollo y evaluación de procesos de oxidación avanzada para el tratamiento de aguas residuales papeleras / Development and assessment of advanced oxidation processes for the treatment of pulp and paper mill effluents

Noemí Merayo Cuevas

Doctoral Thesis in Chemical Engineering, Madrid 2014

ÁNGELES BLANCO SUÁREZ Y MARÍA DAPHNE HERMOSILLA REDONDO, PROFESORA TITULAR DEL DEPARTAMENTO DE INGENIERÍA QUÍMICA E INVESTIGADOR DOCTOR, RESPECTIVAMENTE, DE LA FACULTAD DE CIENCIAS QUÍMICAS DE LA UNIVERSIDAD COMPLUTENSE DE MADRID

INFORMAN

Que el trabajo de investigación titulado "DESARROLLO Y EVALUACIÓN DE PROCESOS DE OXIDACIÓN AVANZADA PARA EL TRATAMIENTO DE AGUAS RESIDUALES PAPELERAS / DEVELOPMENT AND ASSESSMENT OF ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF PULP AND PAPER MILL EFFLUENTS", ha sido realizado bajo su dirección en el Departamento de Ingeniería Química, dentro del Grupo de Investigación de Celulosa y Papel de la Universidad Complutense de Madrid, y constituye la memoria que presenta Dña. Noemí Merayo Cuevas para optar al Grado de Doctor.

Y para que conste a los efectos oportunos, firman la presente, en Madrid a 4 de abril de 2014

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ORIGINAL PUBLICATIONS LIST

[I] D. Hermosilla, **N. Merayo**, A. Gascó, A. Blanco. The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry. A review. Accepted in: *Environmental Science and Pollution Research*.

[II] **N. Merayo**, D. Hermosilla, L. Blanco, L. Cortijo, A. Blanco. Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry. *Journal of Hazardous Materials 262 (2013) 420-427*.

[III] D. Hermosilla, **N. Merayo**, R. Ordóñez, A. Blanco. Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill. *Waste Management 32 (2012) 1236-1243*.

[IV] **N. Merayo**, D. Hermosilla, B. Jefferson, A. Blanco. Alkalinity influence on photo-assisted processes efficiency and catalyst behaviour. Sent to: *Chemical Engineering & Technology*.

[V] **N. Merayo,** D. Hermosilla, C. Negro, A. Blanco. On-line FTIR as a novel tool to monitor Fenton process behaviour. *Chemical Engineering Journal 232 (2013) 519–526*.

[VI] **N. Merayo**, D. Hermosilla, L. Cortijo, A. Blanco. Optimization of Fenton treatment of 1,4-dioxane applying on-line control of the reaction. *Journal of Hazardous Materials 268 (2014) 102-109,*

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SUMMARY

The pulp and paper industry is characterized by being water intensive [1] although important efforts have been carried out to reduce water consumption. The greater the closure of water loops, the greater the accumulation of pollutants in the process circuits. As a result of this accumulation, total water circuits closure is not always the best option and the reclamation of the effluent is the current trend. In addition, different kinds of pollutants are present in the effluents related to the pulp and paper processes, which will influence the efficiency of the treatments. Thus, the best treatment trains must be evaluated in each particular case.

Kraft pulp mill wastewaters are usually difficult to biodegrade as they are characterized by the presence of toxic and bio-recalcitrant compounds. As a consequence, pre-treatments are needed to ensure a high efficiency in the biological stage. However, effluents from paper mills using recovered paper as raw material are characterized by the presence of more biodegradable products [2]. Both effluents are characterized by a high water quality demand. Because of this, such mills cannot work efficiently with total closure of the water circuits. Therefore, the reclamation of the effluent is the next step that must be performed to further reduce water consumption.

Pulp and paper mill effluents have been treated by advanced oxidation processes (AOPs) in order to remove the bio-recalcitrant compounds and, thus, improve the water biodegradability [3]. Ozonation and photocatalysis have been studied for pulp and paper mill wastewaters as they allow the successful treatment of high wastewater volumes. Fenton processes have also been studied as there is a great knowledge of them. One of the main limitations of the AOPs for their implementation at industrial scale is that the efficiency of these treatments varies and is difficult to predict depending on the pollutants which are present in the wastewater. These processes are for example limited by the inhibitory effect of some substances commonly found in industrial effluents, such as carbonates [4]. Therefore, it is necessary to identify and to optimize the best combination of treatments for pulp and paper mill wastewaters in order to achieve the greatest efficiency at the minimum costs.

On the other hand, an alternative to reclaim recycled paper mill effluents includes a reverse osmosis (RO) process, in which silica should be efficiently removed to work at high recoveries without membrane fouling [5]. RO retentates are characterized by a high concentration of bio-recalcitrant pollutants. Hence, their treatment with AOPs is a good alternative for the reduction of the pollutant load of these streams.

Another important limitation in the industrial application of AOPs is their optimum monitoring and control, which is performed through the measurement of some water

quality parameters at certain time intervals. Therefore, new on-line methodologies to monitor AOPs must be developed in order to achieve a rapid optimization of the oxidation processes, to reduce costs and, also, to improve the knowledge about the reactions and degradation mechanisms involved in the treatment of different pollutants.

The main objective of this doctoral thesis is to generate new knowledge on the applicability of AOPs to help papermakers to further reduce the pollution load of pulp and paper industry wastewaters. The optimization of the water treatments will improve the process water quality, the load of the final effluents and the final environmental impact.

During the thesis, the strong influence of the wastewater composition on the efficiency of AOPs was determined [6]. By applying ozone treatment, the kraft pulp mill effluent achieved higher CODs removals (57%) due to its characteristics compared with recycled paper mill effluent (35%). Secondly, the high biodegradability of the recycled paper mill effluent made its treatment viable by a membrane bioreactor obtaining an 80% CODs reduction. Different combinations of biological and AOPs were checked in order to improve the water quality for its possible reuse as fresh water. As a result, only by applying the MBR treatment followed by the ozone post-treatment was possible to improve the efficiency, with a total 90% CODs reduction.

The characteristics of the RO retentate obtained after treating a paper mill wastewater in a treatment chain (anaerobic + aerobic + ultrafiltration + RO), required its treatment by AOPs because of its lack of biodegradable organic matter [7]. The photo-Fenton process achieved a 100% removal of the CODs and TOC, and conventional Fenton was able to achieve more than 60% CODs reduction with an initial neutral pH of the sample.

The influence of alkalinity on photocatalysed processes was also determined in this thesis. It revealed that the effect of the carbonates on the process efficiency was caused by the changes produced by the catalyst's behaviour. The TiO_2 catalyst acts by adsorbing compounds on the catalyst surface and Fe^0 acts through an oxidative process on its surface. Therefore, aggregation of the catalyst produced by the carbonates presence affects TiO_2 photocatalysis process more than it does to Fe^0 photo-Fenton process.

Finally, it has been proved that the FTIR technology is an useful and effective tool to monitor the oxidation processes [8,9]. The developed methodology using an on-line FTIR achieved a significant reduction in the analysis time in comparison with other methodologies. In addition, it allowed to determine the mechanisms involved in the oxidation reactions. The real time information can improve the control over the effect of the reagents, thus achieving an accurate optimization of the process to

degrade recalcitrant compounds and to increase biodegradable substances. The methodology was validated with a model compound, phenol which degradation mechanism is very well known. The final objective is to use this methodology to on-line control the industrial wastewaters treated by AOPs, unfortunately so far this has not been successful. However, it has been satisfactorily applied to monitor a priority pollutant commonly found in industrial wastewaters, 1,4-dioxane which can appear in pulp and paper mill effluents. Furthermore, what has been achieved in this thesis is to clarify the process of its degradation mechanisms which is indeed no longer an issue, since the results have allowed to identify and to clarify the degradation route of this compound, contributing to the state of the art of its removal from wastewaters.

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RESUMEN EXTENDIDO

Uno de los principales problemas medio ambientales en la industria papelera ha sido su elevado consumo de agua [1], y continúa siéndolo a pesar de los muchos avances realizados. Estos avances se han llevado a cabo mediante el cierre de los circuitos de agua, lo que supone la acumulación de contaminantes recalcitrantes en las aguas de proceso. Debido a esta acumulación, el cierre total de los circuitos de agua no siempre es la mejor alternativa, lo cual conduce a la investigación y aplicación de nuevas soluciones, que permiten la reutilización del efluente. La eliminación de los contaminantes es necesaria para evitar problemas en el proceso, en la calidad del producto final y para minimizar el impacto medio ambiental de los vertidos finales.

Dado que los tratamientos biológicos no son capaces de eliminar los compuestos recalcitrantes presentes en las aguas residuales, es necesario estudiar otro tipo de procesos, por ejemplo, los procesos de oxidación avanzada (POAs) y de membranas, los cuales consiguen eliminar dichos compuestos y aumentar la efectividad de posteriores tratamientos biológicos, si bien su coste limita en ocasiones su aplicación.

Un factor muy importante que debe ser considerado antes de abordar el tratamiento de aguas residuales papeleras es el hecho de que las fábricas de pasta y papel son muy diversas, así como los contaminantes presentes en sus efluentes, los cuales dependerán del tipo de proceso empleado, del producto que estén fabricando y de las materias primas utilizadas. Por lo tanto, las características específicas de las aguas residuales, así como los objetivos de la planta en cuanto a su reutilización o vertido, determinarán la combinación óptima de tratamientos y, en consecuencia, la viabilidad industrial de cada combinación debe ser demostrada para cada caso.

Las aguas residuales procedentes de fábricas de pasta kraft se caracterizan por su baja biodegradabilidad, la cual es debida a la presencia de compuestos tóxicos y biorecalcitrantes. Por este motivo, se hacen necesarios pretratamientos que aseguren una elevada eficiencia en los tratamientos biológicos. Por otro lado, los efluentes de las fábricas que emplean papel recuperado como materia prima se caracterizan por la presencia de compuestos más biodegradables [2]. Estos tipos de fábricas no pueden cerrar totalmente los circuitos de aguas debido a los altos requisitos de calidad en el agua de proceso y por lo tanto, la recuperación del efluente es el siguiente paso para reducir el consumo de agua de alimentación necesario para la planta. Los últimos estudios sobre la regeneración de estos efluentes se han centrado en el proceso de ósmosis inversa (OI), el cual permite alcanzar los requisitos de calidad necesarios en el agua tratada. Sin embargo, el proceso de OI está limitado por la eliminación previa de sílice y por la generación de

unos rechazos que se caracterizan por una elevada concentración de contaminantes, generalmente biorecalcitrantes [3]. El tratamiento con POAs de estos concentrados es una buena alternativa para conseguir reducir su contaminación.

El estado del arte muestra que los efluentes de la industria papelera se han tratado con POAs para eliminar los compuestos biorecalcitrantes e incrementar la biodegradabilidad del agua [4]. La aplicación del tratamiento con ozono y del proceso de fotocatálisis se ha estudiado en la industria papelera por sus importantes ventajas, entre ellas la posibilidad de tratar grandes volúmenes de agua, además de evitar en gran medida el acondicionamiento de los efluentes. La gran ventaja de los procesos Fenton es que se han estudiado ampliamente y son bien conocidos, sin embargo, su efectividad es mayor a pH ácido y la producción de lodo de hierro limita su uso en el tratamiento de aguas residuales papeleras. En cualquier caso, la implementación de los POAs a escala industrial es complicada ya que su eficiencia depende considerablemente de los contaminantes que han de ser tratados, de la calidad deseada en el agua tratada y, en especial, de los costes asociados a estos procesos. Además, la presencia de ciertas sustancias en las aguas residuales, como es el caso de los carbonatos, puede inhibir su efectividad [5]. Por lo tanto, se hace necesario identificar y optimizar la mejor combinación de tratamientos para las aguas residuales papeleras y obtener mayor eficiencia a menor coste.

Otra limitación en la aplicación industrial de los POAs es su monitorización y control, lo que se lleva a cabo midiendo ciertos parámetros de calidad del agua a determinados intervalos. Debido a esto último, es necesario desarrollar nuevas metodologías para la monitorización en línea de estos procesos, de forma que se consiga una rápida optimización que conlleve una reducción de costes y una mejora del conocimiento sobre las reacciones y mecanismos de degradación que intervienen en el tratamiento de los contaminantes.

El objetivo general de esta tesis doctoral es aportar nuevos conocimientos que permitan la aplicación de las tecnologías de oxidación avanzada para conseguir reducir la contaminación de las aguas de la industria papelera repercutiendo en una importante mejora de calidad de las aguas de proceso y de los efluentes generados. Durante este trabajo se ha investigado las mejores combinaciones de tratamientos, el efecto de sustancias que inhiben estos procesos y se han buscado nuevas herramientas para el estudio y monitorización de las reacciones de oxidación avanzada.

La viabilidad de los POAs para el tratamiento de efluentes de la industria papelera depende en gran medida de la composición de las aguas residuales [6]. Si éstas son biodegradables y tienen compuestos recalcitrantes a los POAs, la

combinación con tratamientos biológicos mejorará la calidad del agua reduciendo los costes de tratamiento.

De los dos efluentes papeleros estudiados, el efluente procedente de la fabricación de pasta kraft obtuvo mejores resultados que el efluente de la fábrica de papel reciclado cuando estos fueron tratados mediante oxidación avanzada. El tratamiento con ozono eliminó un 57% de la demanda química de oxígeno (DQO) en el caso del efluente procedente de la fábrica de pasta kraft y un 35% en el caso del efluente de la fábrica de papel reciclado. La eliminación de DQO aplicando el tratamiento de fotocatálisis con TiO_2 fue menor en ambos casos: 28% para el efluente de la fábrica de pasta kraft y 24% para el efluente de la fábrica de papel reciclado.

El efluente de la fábrica de papel reciclado fue tratado en un biorreactor de membrana (BRM) debido a su elevada biodegradabilidad. Este tratamiento consiguió una gran reducción de la materia orgánica que resultó en un 80% de eliminación de DQO. Se estudiaron diversas combinaciones de POAs con el tratamiento biológico para incrementar el ratio de degradación, pero sólo la combinación de BRM con un post-tratamiento de ozono consiguió mejorar los resultados obtenidos. La combinación BRM-O_3 alcanzó eliminaciones del 90 y 93% de DQO y color, respectivamente, aumentando la biodegradabilidad del efluente en más del 10%, medido como ácidos grasos volátiles, y posibilitando su recirculación una vez tratado al BRM.

El tratamiento mediante fotocatálisis con TiO_2 de los rechazos de OI no consiguió eliminaciones de DQO tan elevadas como las que se alcanzaron cuando se aplicó el tratamiento Fenton o foto-Fenton [7]. El más efectivo fue el proceso foto-Fenton, que eliminó el 100% de la DQO y del carbono orgánico total (COT). Además, aunque las mayores eliminaciones se obtuvieron cuando los rechazos de OI tratados mediante el proceso Fenton y foto-Fenton se ajustaron a un pH inicial de 2.8, en el caso del proceso Fenton convencional se consiguieron eliminaciones aceptables de la DQO (>60%) sin necesidad de ajustar el pH inicial del agua (7.5).

El tratamiento de fotocatálisis con TiO_2 aumentó la biodegradabilidad de los rechazos de OI lo suficiente para considerar su combinación con una etapa biológica posterior, de manera que se consiga un aumento de la eliminación de DQO final.

También se ha realizado un estudio acerca de la influencia de la alcalinidad en los procesos fotocatalizados y su efecto sobre el catalizador, ya que la presencia de carbonatos es muy común en las aguas residuales papeleras y su efecto sobre los POAs todavía no es claro en la literatura. Dependiendo del proceso, los efectos observados fueron diferentes y esto se debe principalmente al efecto que los carbonatos tienen sobre el comportamiento del catalizador. El tratamiento de fotocatálisis con TiO_2 mostró una reducción importante de la eficiencia al tratar una

disolución de lignina en presencia de bicarbonatos. El mecanismo de fotocatálisis con TiO_2 está basado en la adsorción de los compuestos en la superficie del catalizador antes de que estos sean oxidados. La presencia de carbonatos dio lugar a modificaciones de pH y a un incremento de la fuerza iónica del medio, lo cual favoreció la agregación del TiO_2 contribuyendo a la disminución de la eficiencia del proceso ya que la superficie disponible para la etapa de adsorción era menor. La presencia de carbonatos tuvo poca influencia sobre la eficiencia del proceso foto-Fenton con Fe^0 como catalizador heterogéneo. En este caso, el mecanismo está basado principalmente en el proceso oxidativo en la superficie del catalizador y la presencia de carbonatos no afectó significativamente a este proceso, a pesar de que el aumento de la fuerza iónica debido a la adición de carbonatos dio lugar a una cierta agregación.

Por último, se evaluó y desarrolló una nueva metodología basada en una sonda comercial de FTIR para el control y la optimización en línea de los POAs [8,9]. Este control en línea durante el tratamiento con POAs permite optimizar estos procesos para degradar los compuestos recalcitrantes y obtener la mayor cantidad de compuestos biodegradables al final del tratamiento con el mínimo consumo posible. De esta forma, la combinación de los POAs con procesos biológicos durante el tratamiento de efluentes papeleros será óptima. Se comprobó que la sonda FTIR fue efectiva para estudiar y optimizar la oxidación Fenton de compuestos modelo, en este caso el fenol. Los resultados obtenidos se validaron mediante análisis cromatográficos y los mecanismos obtenidos coincidieron con lo esperado, en base a la amplia literatura publicada para la degradación del fenol. Se concluyó que la tecnología FTIR puede utilizarse para evaluar procesos de oxidación satisfactoriamente, reduciendo el tiempo necesario para el análisis en comparación con otras metodologías. La aplicación en línea de esta herramienta permitiría una rápida optimización del tratamiento minimizando los costes.

Esta metodología se utilizó en línea durante el tratamiento de oxidación avanzada de un agua industrial papelera. Desafortunadamente no fue posible la evaluación del proceso debido al límite de sensibilidad de la sonda FTIR. Sin embargo, esta metodología se aplicó con éxito para el seguimiento de compuestos prioritarios. En concreto se utilizó para estudiar el mecanismo de degradación del 1,4-dioxano. Este compuesto puede aparecer en los efluentes papeleros dependiendo del proceso de fabricación. El 1,4-dioxano fue completamente eliminado mediante el tratamiento Fenton mientras que los compuestos orgánicos alifáticos no se degradaron con este tipo de tratamiento, como era de esperar. El equipo permite determinar en qué momento de la reacción se han formado compuestos más biodegradables, los cuales pueden ser sometidos a tratamientos biológicos convencionales (por ejemplo: ácido oxálico, ácido acético, etilenglicol) permitiendo disminuir los costes del proceso global.

Las aportaciones fundamentales de esta tesis han sido: el desarrollo de sistemas de tratamiento avanzado y la identificación de las posibles combinaciones que permiten un mayor cierre de los circuitos de agua de proceso en la industria papelera; la realización de bancos de ensayo en industrias del sector papelero para el análisis de la viabilidad de POAs y su combinación con tratamientos biológicos; el tratamiento eficaz de corrientes de rechazos en los que se elimina la materia disuelta y coloidal recalcitrante mediante POAs y se favorece su posterior tratamiento biológico; el estudio de los mecanismos de interacción de la alcalinidad con catalizadores heterogéneos empleados en procesos fotocatalíticos de oxidación avanzada; el desarrollo de una metodología para la monitorización de los POAs; y la eliminación de contaminantes prioritarios que pueden estar presentes en efluentes de la industria papelera, fenol y 1,4-dioxano, para conseguir optimizar el proceso Fenton y determinar sus mecanismos de degradación con la tecnología FTIR en línea.

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1 INTRODUCTION

1.1. Water use in pulp and paper processes

Paper is characterized for being a natural, renewable and recyclable product, which makes the paper cycle sustainable. Pulp and paper industry is one of the most relevant industrial sectors in Spain with 3400 million euro of annual turnover and more than 17400 direct jobs in 95 industrial plants. During 2012 Spain produced 2 million tons of pulp and more than 6 million tons of paper and cardboard (Aspapel, 2013). Kraft process is the most extended pulp production process (around 80% of the total pulp produced in Europe; (IPPC, 2013)). In addition, Spain is characterized by the extent of recycled products manufactured, 82.3% of the total production (Aspapel, 2013). Among the recycled products, packing papers are the majority (65.9% of the European recycled products; CEPI, 2012), and their quality requirements allow working with closed water loops (IPPC, 2013). Other types of recycled paper do not allow working with zero effluent discharge due to higher

quality requirements, such as household papers (6.8%) and graphic papers (24.1%) (CEPI, 2012). Pulp and paper industry is a water intensive consumer (Buyukkamaci and Koken, 2010), consequently several drivers impulse this sector to reduce its water consumption. Among others, water stress, legal requirements, environmental concerns and, indeed, the potential benefits are the main ones. Water scarcity is, however, more important in countries which suffer from water shortages, such as Spain.

Many different types of papers can be manufactured in different processes using various types of raw materials, generally wood, recovered paper and agricultural sources. Pulp and papermaking processes are based on turning the fibrous raw material into pulp, which can be made by mechanical, semichemical and chemical methods. Once the pulp is obtained, it is washed and, if required, bleached. The paper sheets are produced from a diluted pulp suspension (commonly 1% consistency (10 $g{\cdot}L^{-1}$) is used), which is subjected to drainage, press and dry operations. Pulp and paper production exists in separate mills (non-integrated) or as a unique mill (integrated).

The virgin pulp manufacturing processes consist of isolating the cellulose fibres from the rest of the wood components. In kraft pulp manufacturing process, the chopped wood is handled using water and treated within digesters along with sodium hydroxide and sodium sulphide used to dissolve the lignin and release the fibres. Lignin is a compound responsible for the union of cellulose fibres and for the dark colour of paper. Removal of lignin during the kraft pulp process is usually performed with oxygen in closed water circuits, although an important amount of lignin is also removed in washing and bleaching stages. This pulp, consisting of fibres and cooking liquor, is washed with water in order to remove the liquor, which is sent to the chemical products reclamation plant. The washing step is focused on removing the maximum amount of liquor-dissolved solids from the pulp, using as little water as possible. The dissolved solids in the pulp are removed because they interfere with the bleaching and papermaking processes, increasing production costs (Bajpai, 2010). The pulp is then bleached using elemental chlorine free (ECF) or totally chlorine free (TCF) as bleaching methods.

At the end of the kraft pulp process, purification and pressing processes are applied. The purification allows the removal of unwanted materials, such as splinters or heavy particles (uncooked). The final pulp suspension is diluted and directly used in the paper machine if pulp and paper manufacture is integrated. However, if the production process only includes pulp manufacture, the pulp must be pressed and dried to remove the water, cut in sheets, packed in bales, stored and sent to the paper mills.

Kraft pulp mill effluents contain carboxylic acids, nutrients, suspended solids, salts from the wood and coloured substances and they are characterized by certain

toxicity due to the presence of lignin, toxic extractive compounds, such as resin acids, chloride compounds from the bleaching stage (if chloride compounds are used) and metals. This toxicity can affect the biological treatments. Even if biological treatments work properly, sometimes they are not economically viable in small mills and their efficiency is limited below 50% (IPPC, 2013). Therefore, treatments to increase the biodegradability of these effluents are still needed. Among the toxic compounds found in these effluents, lignin is the main constituent of chemical oxygen demand (COD) and the main factor contributing to colour. Its decomposition can result in toxic by-products (Makhotkina et al., 2008) due to the structure of lignin, which is a polymer formed by aromatic units, principally phenolic ones. The complex organic structures, such as those containing lignin or chlorine, can be broken down into simpler and more biodegradable compounds through the action of hydroxyl radicals (OH·) (Balcioglu et al., 2003; Bigda, 1995; Mansilla et al., 1997).

When obtained from recovered paper, the pulp manufacturing process is different. Recovered paper is selected and classified according to its quality. The pulp is prepared in a pulper by desintegrating the mixture of recovered paper in water. Chemical products (hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), silicates, soap) are commonly added, depending on the product and production process. A mechanical separation of the impurities is conducted based on the differences between physical characteristics of the fibres and pollutants, such as their size and density. The recycled pulp must be deinked when whiteness is important, such as in the case of graphic paper. This purification is usually made by flotation systems using chemical products like surfactants. Bleaching can be performed if necessary by the addition of chemicals (H_2O_2, hydrosulphite or others). At the end of the process, the pulp is stored before it goes into the paper machine. During this storage, the addition of additives is made in order to adjust the composition, tone and other properties. The consistency is also adjusted by dilution for optimal sheet formation in the paper machine. Once the paper is formed, water is removed by drainage, pressing and drying. The paper goes then to the finishing (sizing, coating and calender) and converting section. Fresh water is used at the paper machine to ensure the water quality requirements in that part of the process. Water is used in counterflow to the materials flow.

Effluents from recovered paper production are characterized by the presence of suspended solids, organic substances, such as starch derivates, chloride organic compounds (if bleaching is made with chlorine derivatives), nutrients, metals, salts and coloured substances; being these effluents more biodegradable than those from processes that use virgin fibres (Thompson et al., 2001). A qualitative contribution of pollutants depending on the raw materials used in the process is shown in Table 1.

Table 1. Contribution to the process water pollution by main fibrous raw materials (Negro et al., 1995).

	Fine particles content	Inorganic matter content	Soluble organic matter content	Microorganism content
Mechanical pulp	++++	+	++++	++
Bleached chemical pulp	+	+	++	+
Not deinked recycled pulp	+++	++++	+++	++++
Deinked recycled pulp	++	+++	+	++

In pulp and paper production, minimization of water consumption imply a strategic management aimed to the conservation of the water and the reuse and recycling of used process waters in an attempt to minimize both water consumption and effluent discharge (Gavrilescu et al., 2008) (Figure 1). More restrictive legislation has increased efforts towards better water preservation and effluent load reduction in the manufacturing process. The work during the last decades has been focused on the identification of the most economically effective processes, the development of wastewater treatment and the optimization of the process design. In order to reduce the water consumption, two basic strategies have been used: the modification of the individual processes and its units to reduce the inherent water needed; or the water reuse looking for opportunities to reuse the outlet stream of one operation process as the inlet stream of the same operation process or of another one. In this way more than 40% water intake reduction has been achieved since 1990 (CEPI, 2013).

In spite of all the efforts carried out to minimized water consumption, this sector is still water intensive since water is required for dispersion and transport of the fibrous raw materials and additives throughout the different stages of the production process, as heat-exchange fluid, as sealant in vacuum systems, as steam and as lubricant (Ordoñez et al., 2009). In modern mills where best available technologies are applied, the average water-use range is from 3 to 10 $m^3 \cdot t^{-1}$ depending on the product quality, although some paper products, such as tissue, have a higher range.

1.5-3 $m^3 \cdot t^{-1}$ is required for board products in closed systems, 5-15 $m^3 \cdot t^{-1}$ for newsprint, 15-20 $m^3 \cdot t^{-1}$ for tissue and more than 20 $m^3 \cdot t^{-1}$ for high quality printing grades and speciality papers (IPPC, 2013).

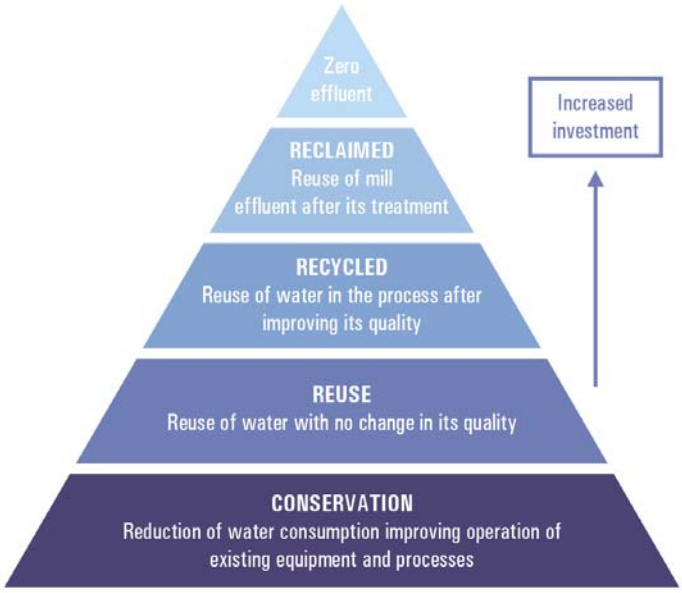

Figure 1. Total water management.

Although the closure of circuits has several benefits, such as less water consumption, less fresh water pre-treatment, lower volume to effluent treatment, decrease fibre and filler losses and reduce energy demand, it implies the accumulation of pollutants in the process water. Figure 2 shows that there is a break point in the accumulation of contaminants that limits the closure of the water circuits. Contaminants must be removed before further closing the water circuit so as not to produce problems, such as corrosion, clogging of equipment, scaling and slime forming in the process or in the final product. In order to reuse process water, internal treatments are installed to remove these substances (CAR/PL, 2005). The main advantage of in-line treatment is that only a part of the COD load from the purge of white water needs to be eliminated to keep the level of contaminants in the circuit low, making the treatment economically attractive (IPPC, 2013). There are several processes commonly used to treat the internal streams and the final

effluents in the pulp and paper industry. Figure 3 shows some of them and the qualitative yields for the removal of the main pollutants present in the wastewaters.

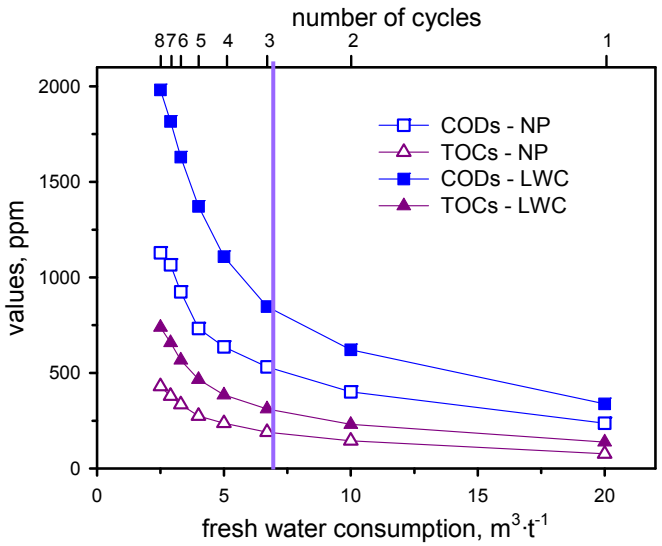

Figure 2. Dissolved COD and TOC accumulation (NP: newsprint; LWC: light weight coated) (Miranda et al., 2009a).

Several methods can be used to remove pollutants. Phisical and chemical methods are commonly used as internal water treatments as they remove solids efficiently. Dissolved air flotation (DAF) is the most common one because DAF treats large water flows with a wide range of solids content at a low cost. The efficiency of DAF units can be enhanced by coagulation-flocculation processes. Most of the pollutants in pulp and paper mill streams are colloidal and negatively charged. Through coagulation process, colloidal particles are destabilized and the forces between them are removed. A subsequent flocculation process aggregates destabilized particles easily, forming bigger flocs for flotation or, in some cases, for sedimentation (Ordoñez, 2012). Although DAF units can efficiently remove 80-98% of suspended solids and can agglomerate and remove finely dispersed and colloidal organic particles, there is a limit of around 20% for the reduction of dissolved organic matter, measured as COD (Miranda et al., 2009b).

Regarding membrane processes, ultrafiltration (UF) is widely used for internal treatments and in water reclamation plants when the water quality requirements are

high. However, the characteristics of the inlet wastewater must be taken into account and a concentrated effluent must be disposed of. UF combined with RO can be used to remove the salts and to recycle the biological effluent although there are several limitations, like in deinking mills due to the possible fouling of RO membranes in effluents with high silica concentration.

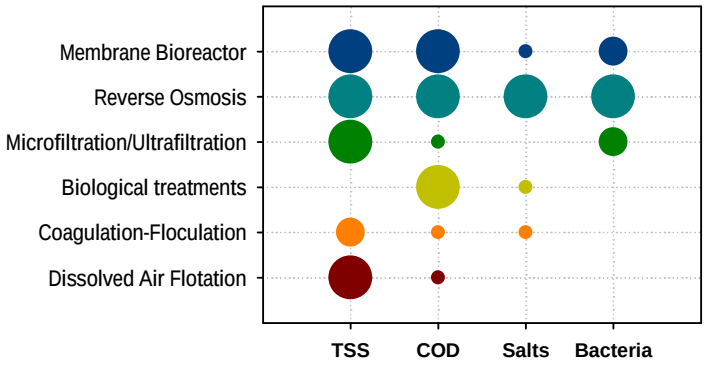

Figure 3. Qualitative pollutants removal yields according to the water treatment applied (Addapted from: Ordoñez, 2012).

The application of biological processes may involve anaerobic treatment followed by aerobic in order to achieve the complete removal of biodegradable organic matter and the recovery of energy. These biological treatments are relatively inexpensive, although they cannot be applied when toxic compounds are present and their efficiency will be reduced by the presence of biorecalcitrant compounds. Furthermore their implementation depends on the size of the plant. Precipitation and scaling of calcium carbonate can be the limitation for reusing biologically treated water as process water because the potential of precipitation in pulp and paper water streams is especially high. This precipitation can be avoided by the use of chemical additives, such as precipitation inhibitors, or lowering the calcium concentration by controlled precipitation of calcium carbonate (IPPC, 2013).

The current goal in water management in pulp and paper industry is to further reduce fresh water consumption by improving the mill's circuit closure, without interfering with the runnability of the machine and without affecting the paper quality. Therefore, this industrial sector needs to employ advanced water treatment technologies to reclaim and reuse the mill effluent (IPPC, 2013; Koppol et al., 2003).

1.2. Membrane bioreactor technology

Membrane bioreactor (MBR) is a compact purification system that joins an activated sludge treatment and an UF membrane. Inlet effluent is introduced into an aerated bioreactor where organic compounds are oxidized by the activated sludge. The water is separated from the sludge when the aqueous suspension passes through the macro or UF membrane. The sludge is returned to the bioreactor and the permeate is discharged or reused as particle free effluent.

There are two basic MBR configurations, submerged or sidestream filtration (Simstich and Oeller, 2010). The sidestream configuration has tubular membrane modules outside of the bioreactor that are located horizontally or vertically and the rejected stream is returned to the bioreactor. For the submerged configuration, the membranes are inside the bioreactor, located vertically (hollow fibres or flat sheets) or horizontally (hollow fibres). These systems are aerated from the bottom and the permeate is removed by suction.

Some of the main advantages of MBR over conventional biological treatments are the high biosolids concentrations due to the high efficiency of membranes in the separation process, lower residence time in the reactor and, consequently, lower volume required due to the high biomass concentration (Ragona and Hall, 1998; Stahl et al., 2004). Another advantage is the decoupling of solid retention time and hydraulic retention time, thus achieving higher sludge ages (more than 10 days (Meng et al., 2009)) which promote a higher degradation of slowly biodegradable compounds. In addition, MBR shows superior effluent quality, the excess of sludge production is reduced and there is the option of independence between system operation and sludge sedimentation capacity (Dialynas and Diamadopoulos, 2008). As a consequence, this technology can be considered a sustainable recycled practice for the pulp and paper industry (Galil and Livinsky, 2007; IPPC, 2013).

Even though MBR has demonstrated many advantages over conventional biological processes and also over conventional UF, such as the reduction of fouling, and it has been used to treat paper mill effluents (Ordoñez, 2010), this process can achieve very good synergies in new treatment trains in combination with advanced oxidation for the regeneration of pulp and paper mill effluents.

1.3. Advanced oxidation treatments

Advanced oxidation processes (AOPs) are based on the formation of OH· in sufficient concentration to chemically oxidize the pollutants (Glaze et al., 1987). OH· are almost twice as reactive as chlorides and their oxidation potential is close to that of fluoride (E = 2.32 V/NHE at pH = 7) (Bigda, 1995). These radicals start the

destructive oxidation of the organic substances (R) of wastewater through reactions 1 and 2, as detailed below (Huang et al., 1993).

a) OH· addition reaction

$OH\cdot + R \rightarrow ROH\cdot \rightarrow$ hydroxylated products $\quad K \approx 10^{7}\text{-}10^{10}\ M^{-1}s^{-1}$ (1)

b) Hydrogen atom abstraction

$OH\cdot + R \rightarrow R\cdot + H_2O \rightarrow$ oxidized products $\quad K \approx 10^{7}\text{-}10^{10}\ M^{-1}s^{-1}$ (2)

Organic free radicals are formed as intermediates and are further oxidized by other intermediates to form stable oxidized products (Huang et al., 1993).

Total oxidation of organic compounds could be neither the optimum solution nor economically viable due to the high energy demand and the quantity of chemicals needed. However, the OH· can be used to produce the partial oxidation of non biodegradable organic compounds like lignin and, consequently, effluent biodegradability would increase (Balcioglu et al., 2007; Bijan and Mohseni, 2008; Chang et al., 2004; Mounteer et al., 2007). Therefore, the partial direct oxidation and the subsequent biodegradability increase may be the key for a complete COD removal in a post-biological treatment at feasible cost (Simstich and Oeller, 2010).

The application of AOPs to pulp and paper mill effluents is influenced by the wastewater composition (type of organic load, salts presence e.g. alkalinity and chlorides). Therefore, its application has to consider the technical and economical viability based on the wastewater composition since it affects the economic figures (De Laat et al., 2004). Commonly, pulp and paper industry effluents are characterized by their high alkalinity due to the addition of calcium carbonate as one of the fillers in the fabrication process (Ordoñez et al., 2011). The presence of carbonates (HCO_3^-/CO_3^{2-}) may have a scavenger effect on AOPs, although reported results are contradictory. Some authors propose that carbonates have a positive effect on the AOPs of different substances (Epling and Lin, 2002; Kumar and Mathur, 2006; Lair et al., 2008; Zhang et al., 2009), while other authors report an inhibitory effect of carbonates (Bhatkhande et al., 2004; Guillard et al., 2003; Pujara et al., 2007; Zhu et al., 2006). On the other hand, the presence of volatile organic acids may also influence the efficiency of the AOP as they may be resistant to the oxidation processes consuming OH· (Merayo et al., 2013a).

There are several AOPs that have been applied for the treatment of pulp and paper mill effluents. From those available, ozonation, TiO_2 photocatalysis and Fenton processes are the most studied due to their industrial maturity and lower costs. Their main advantages and drawbacks are shown in Table 2.

Table 2. Comparison of drawbacks and advantages for some AOPs.

	Ozonation	TiO_2-photo-catalysis	Fenton	Photo-Fenton
Oxidation mechanism	Directly with O_3 or radicals from O_3 decomposition	Directly with UV or radicals from heterogeneous catalysis	Radicals from homogeneous/ heterogeneous catalysis	Directly with UV or radicals from homogeneous/ heterogeneous catalysis
Optimum pH	Basic for radials formation	Point of zero zeta potential	Acid	Acid
Reagents involved	In-situ generated O_3	TiO_2	Fe^{2+}/H_2O_2	Fe^{2+}/H_2O_2
Catalyst recovery and reuse	—	High/Possible	Medium/ Possible	Medium/ Possible
Degree of industrial implementation	Very high	High	Very high	High
Residuals produced	None*	Low	Medium	Low
Energy demand	Medium/high	Very high**	Very low	Medium/Low**

*During ozone treatment if bromine is presented in the wastewater it can be converted into bromate.

**Energy demand in photocatalysis and photo-Fenton treatment can be drastically reduced by the use of the solar energy.

Ozonation process

Ozone can oxidize other compounds through direct reaction with dissolved compounds, in which oxygen atoms are progressively introduced into the compounds, forming smaller molecules with greater percentage of oxygen. This reaction mechanism, ozonolysis, is predominant at low pH and consists of direct electrophilic attack by molecular ozone. It is a selective reaction that leads to the formation of carboxylic acids (Alvares et al., 2000). At high pH, ozone is decomposed to form free radicals, such as OH·, that degrade the organic compounds by non-selective chain reactions. However, pH values above 11 can favour the dissociation of OH· into O^- species (Hoigne and Bader, 1976). The primary reactions of ozone with organic compounds in water are shown in Figure 4 based on direct reaction of ozone and indirect reaction through OH· formed by ozone decomposition. The half life of ozone is short and, as a result, continuous generation of ozone during the process is required. This is one of the main drawbacks of this treatment due to the high costs associated to ozone generation (Catalkaya and Kargi, 2007; Kreetachat et al., 2007).

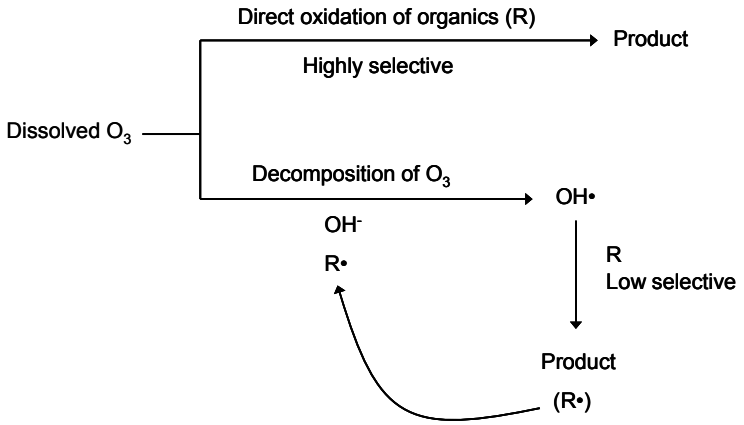

Figure 4. Ozone reactions with organics in water (Addapted from: Alvares et al., 2000; Hoigne and Bader, 1976).

Ozone stability is influenced by pH and salts. There is some controversy about the influence of inorganic anions on AOPs. Generally, losses of treatment efficiency are attributed to inorganic anions and explained by their scavenging effect through the consumption of OH· to generate other radicals with weaker oxidation potentials

(Barndok et al., 2012; Guillard et al., 2003). However, some studies reported that inorganic anions did not affect the ozone process of phenol, such as SO_4^{2-}, Cl^- and NO_3^-, whereas carbonates addition reported an improvement of the efficiency due to the increase of the pH (Barndok et al., 2012). On the other hand, other authors have reported an inhibitory effect of carbonates for the ozonation of humic substances and dyes (Chiang et al., 2006; Song et al., 2008).

Temperature affects solubility of ozone in water, which decreases 2.5 times as temperature increases from 20 to 60 ºC by significantly lower mass transfer of ozone to the aqueous phase. The lower concentration of ozone explains the oxidation rate changes obtained by increasing temperature (Bijan and Mohseni, 2004). In addition, thermal degradation of ozone is increased as the temperature increases (Salokannel et al., 2007). However, the ozonation efficiency between 20 and 60 ºC was not affected treating alkaline bleach plant effluent (Bijan and Mohseni, 2004) or biologically treated pulp and paper mill wastewater (Salokannel et al., 2007). Therefore, the process efficiency can be affected by the efficiency of gas-liquid mass transference, which is low due to the low solubility of ozone in aqueous solutions (Kreetachat et al., 2007), although it depends on the effluent and the temperature range.

Ozonation is considered a feasible method for oxidation of organic pollutants present in the wastewater from pulp and paper mills. Double and triple bonds of lignin compounds responsible for colour are easily oxidized with ozone (Kreetachat et al., 2007). In addition, ozonation usually increases biodegradability of these effluents due to the degradation of toxic compounds and the reduction of molecular weight by breaking down high molecular weight (HMW) fractions into low molecular weight (LMW) ones (Amat et al., 2005b; Balcioglu et al., 2007).

A previous knowledge of organic compounds structure in the effluents is necessary in order to establish the treatment suitability. Ozonation treatment as standalone technology is considered unfeasible in pulp and paper industry and it cannot provide the sufficient removal and mineralization of organic compounds (Bijan and Mohseni, 2008). However, a partial oxidation with ozone to increase wastewater biodegradability may be suitable (Bijan and Mohseni, 2008). An interesting option is its combination with pre-biological or pre-membrane treatments, thus avoiding the oxidation of the LMW fraction (Bijan and Mohseni, 2008).

However, these processes have not been studied deeply comparing their applicability and efficiency in different wastewaters produced in the pulp and paper industry. In addition, the combinations of ozone with biological treatments, specially advanced biological ones, are not extensively studied.

TiO_2 photocatalysis process

Some AOPs are focused on the UV light use with a reusable catalyst, such as TiO_2 (Yeber et al., 2000). These treatments are based on semiconductor irradiation with UV light with wavelengths shorter than 390 nm (Yeber et al., 2000). The electronic structure of the catalyst comprises the highest occupied band full of electrons, the valence band, and the lowest unoccupied band, the conduction band, being the bandgap energy, the difference in energy between the two bands. UV illumination produces electron-hole pairs, which, in one hand, can recombine in the bulk or at the surface of the catalyst, or, on the other hand, can directly or indirectly react at the surface. The photogenerated electron can reduce oxygen or oxidizing intermediates and the photogenerated hole can oxidize organic compounds or oxidized intermediates, which can lead to the mineralization of the pollutant (Parsons, 2004) (Figure 5). Heterogeneous photocatalysis using TiO_2 and UV light has shown efficiency in the treatment of a large number of refractory organic compounds through the generation of electron-hole pairs, such as the case of treating ECF bleaching effluents and lignin containing solutions, in which colour and dissolved organic carbon (DOC) were efficiently removed (Chang et al., 2004; Perez et al., 2001). During oxygen reduction process, radical species, such as OH·, can be formed that further react with any other adsorbed organic molecule (Parsons, 2004). This process can also lead to the final mineralization where CO_2 and H_2O are produced (Ahmed et al., 2010).

Optimum dosage of TiO_2 is a compromise to achieve the maximum catalyst in the solution, to provide the maximum surface to promote the pollutants degradation, and to avoid an excessive amount of catalyst that causes a shadow effect interfering with the transmission of UV light, thus diminishing the generation of electron-hole pairs (Catalkaya and Kargi, 2008; Chang et al., 2004; Tanaka et al., 1999). As a result, studies about the optimum dosage of TiO_2 have been carried out; particularly, 10 $g{\cdot}L^{-1}$ of TiO_2 has been reported the maximum dosage to avoid the shadow effect for the treatment of lignin powder, increasing the efficiency as reaction time increases as well (Chang et al., 2004). On the other hand, optimum conditions treating biologically pretreated pulp and paper mill effluent at basic pH (pH = 11), were 0.75 $g{\cdot}L^{-1}$ of TiO_2 during 60 minutes of reaction, which reached 80% TOC removal (Catalkaya and Kargi, 2008). In addition, neutral pH conditions showed better treatment efficiencies purifying effluents from a newsprint paper mill (Merayo et al., 2013a), as well as they yielded an almost complete decolourization of a kraft pulp mill effluent (Gouvea et al., 2000). The good results achieved at neutral pH are explained by the lower competition of pollutants with anions and cations that are present in lower amount, for the reactive sites on TiO_2 surface. Finally, the treatment of lignin solutions resulted in higher colour removal efficiencies at acid pH than at

neutral ones (Chang et al., 2004) because the cations adsorbed on catalyst surface attract anionic pollutants.

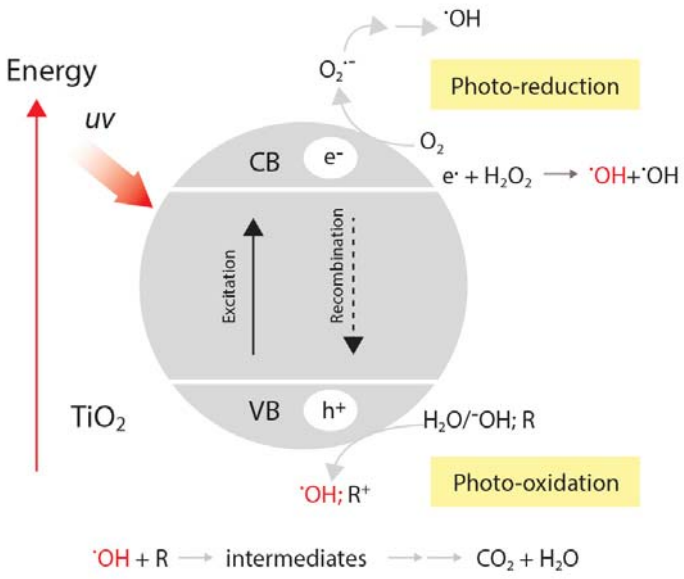

Figure 5. TiO_2 photocatalytic degradation process scheme. (CB: conduction band; VB: valence band).

Several authors (Catalkaya and Kargi, 2008; Yeber et al., 2000) have obtained fast reductions of toxicity and increased biodegradability for different synthetic solutions treated by photocatalysis. Therefore, photocatalytic systems could be also applied as a stage of pre-oxidation prior to a biological treatment (Yeber et al., 2000).

As well as in the ozonation case, a systematic well planned research comparing different wastewaters from pulp and paper mill treated by photocatalysis is still necessary and the possible benefits of its combination with advanced biological processes has to be assessed in order to contribute to increase the knowledge about the best treatment trains for different pulp and paper effluents. Moreover, it is important to establish the influence of some typical compounds found in these wastewaters, such as carbonates, on the treatment efficiency and on the behaviour of the TiO_2 catalyst.

Fenton processes

Fenton treatment is one of the most common AOPs for wastewater treatment. Moreover, it usually implies lower capital costs than other AOPs (Esplugas et al., 2002; Tang, 1996). Fenton treatment is based on the electron transference between H_2O_2 and ferrous iron (Fe^{2+}). Iron acts as a homogeneous catalyst to generate OH· that degrade organic compounds (Harber and Weiss, 1934) as it is expressed in reaction 3.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad K_1 = 70.0\ M^{-1}s^{-1} \qquad (3)$$

Fenton treatment usually happens through four stages (Bigda, 1995): pH adjustment, oxidation reaction, neutralization – coagulation, and precipitation (centrifugation). Organic substances are removed in the oxidation and coagulation stages. The pH is one of the main factors affecting the process due to the optimum value being between 2.5 and 3 because iron solubility and H_2O_2 stability are higher (Hermosilla et al., 2009b). Fenton effectiveness is related to the amount of OH· formed, which depends on the H_2O_2 concentration and the amount of Fe^{2+} available.

Although the Fenton oxidation mechanism of some model pollutants, such as phenol, is well known due to its extensive treatment by AOPs, there is still a lack of information about degradation mechanisms of many other target compounds, such as the case of 1,4-dioxane, which is a priority pollutant usually found in industrial effluents.

The main drawbacks of the Fenton treatment are the acidic pH and the iron sludge produced and managed as a waste product (Pignatello et al., 2006). The amount of iron sludge could be reduced by modifying the conventional process, for example, by using UV light.

The photo-Fenton process has two main characteristics: (a) ferric iron (Fe^{3+}) reduction to Fe^{2+} (reaction 4), generating additional OH· through the photolysis; and (b) photo-decarboxylation of ferric carboxylate (reactions 5 and 6) (Kavitha and Palanivelu, 2004).

$$Fe(III)OH^{2+} + h\nu \rightarrow Fe^{2+} + OH\cdot \qquad (4)$$

$$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R\cdot \qquad (5)$$

$$R\cdot + O_2 \rightarrow RO\cdot_2 \rightarrow \text{Products} \qquad (6)$$

These reactions show that the amount of catalytic iron is reduced during the photo-Fenton process and consequently, the amount of iron sludge could be highly reduced. Moreover, some organic compounds, such as carboxylates, can be treated effectively (Hermosilla et al., 2009b).

In addition, many studies are focused on the application of iron from solid sources in order to use zero valent iron (Fe^0) instead of Fe^{2+}. Heterogeneous reactions are generally much slower at the same mole per litre reagent concentrations, but sometimes more efficient because they consume less peroxide per mole contaminant degraded (Pignatello et al., 2006). Some of the main advantages of using Fe^0 are the cost-savings due to the use of metal iron, the reduction of salts concentration in the medium and, in many cases, the possibility to completely avoid sludge formation (Bremner et al., 2006). Blanco et al. (In progress) achieved 100% CODs removal and 99% TOC removal, treating a synthetic phenol solution with Fe^0 microspheres as catalyst of photo-Fenton process. Moreover, working at neutral pH, they achieved 99% CODs removal treating phenol while the microspheres structure remained unchanged, indicating that the catalyst can be easily recovered.

Although Fenton processes are well known, their application on RO retentates, specially on the ones coming from the pulp and paper industry, are not deeply assessed. In addition, it is important to determine the influence of some considered scavengers present in pulp and paper mill wastewaters on these processes and their catalysts.

1.4. AOPs in combination with biological processes

One of the main drawbacks of AOPs is their high operational costs in comparison to biological treatments. In order to reduce the cost, these processes may be used, as already mentioned, as pre-treatments to increase wastewater biodegradability when bio-recalcitrant compounds are present in the wastewaters. This pre-oxidation treatment may result in the formation of intermediates easily degraded by microorganisms thus greatly increasing the feasibility of the treatment chain.

It is reported that ozone oxidation of bleached kraft pulp wastewaters has achieved an improvement in process efficiency through the combination with biological treatments (Bijan and Mohseni, 2005; 2008; Morais et al., 2008; Mounteer et al., 2007), as well as in the case of photocatalysis (Moraes et al., 2006).

Other appealing possibility consists of an initial removal of LMW load by applying biological or membrane processes and the further treatment of the concentrated stream by oxidation in order to remove the recalcitrant organic matter that was not removed in previous processes. Moreover, the posterior ozonation of these streams increases its biodegradability allowing an effective further bio-treatment (Bijan and Mohseni, 2008; Schlichter et al., 2003). Bio-O_3-Bio and NF-O_3-Bio combinations have ten times lower ozone consumption than the ozonation treatment without pre

or post-treatments due to the selective oxidation of HMW compounds and the effective use of ozone (Bijan and Mohseni, 2008).

The combined processes of pre-ozonation coupled with biofiltration are proposed by CAR/PL (2005) and IPPC (2013) as an alternative treatment of wastewater from paper grades that contain poorly biodegradable COD. It is proved that this advanced treatment of the effluent achieves a meaningful reduction of the COD, AOX and colour with minimum dosages of ozone. The main objective in this case is to turn wastewater complex organic pollutants into partial biodegradable compounds. Figure 6 shows an outline of the combined treatment, in which the tests in several mills have shown reductions of up to 50% of initial COD. Efficiency of the ozone treatment depends on the water quality and the specific treatment system and, therefore, there is no general conclusion and the results cannot be extrapolated to any other wastewater.

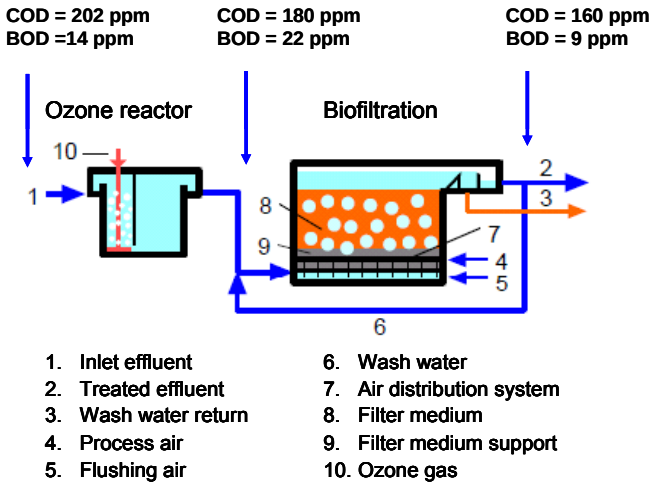

Figure 6. Ozonation and post-biofiltration combined process (CAR/PL, 2005; IPPC, 2013).

Photocatalysis might be also considered an interesting alternative for pre- or post- biological treatment stages. For example, at lab scale, the relative quantity of HMW compounds considerably decreased (< 30%) in a kraft bleaching effluent subjected to supported photocatalytic treatments, producing a higher content of LMW species (Yeber et al., 2000). In fact, the application of photocatalysis as post-biological treatment achieved a 75% colour removal in the treatment of black liquor,

which is 15 times higher than the resulting decolourization after a standalone photochemical process; in addition mineralization was enhanced up to 140% with respect to the previous biological stage. In addition, 45% mineralization enhancement was also reported in this laboratory essay for the pre-biological treatment of kraft effluent by photocatalysis (Moraes et al., 2006).

Solar photo-Fenton treatment has achieved very good particular COD removal results (90% after a 2h-process) in the treatment of biologically pre-treated pulp and paper mill wastewater (Gomathi and Kanmani, 2006). This improvement may be attributed to the previous removal of biodegradable material in the biological stages of the treatment train; whereas directly treating the raw wastewater mixture of contaminants would have reduced the efficiency of the solar photo-Fenton process because certain oxidative power would have been lost trying to degrade biodegradable organic compounds recalcitrant to oxidation.

In summary, the combination between AOPs and biological treatments must be extensively studied, especially in the case of industrial wastewaters, whose particular characteristics can determine better synergies for one combination instead of another one.

1.5. Wastewater treatment optimization and control

The efficiency of the wastewater treatment plant depends on the water quality, the treatment chain and the optimization of the operational parameters. If the treatment plant is not well controlled, the quality of the final effluent will be affected. Therefore, the main operational parameters must be checked during the operational phase of industrial wastewater treatment systems. This evaluation can be made by implementing a monitoring programme, which would allow the establishment of operational strategies in the treatment system. The operational control is important for the optimization of operational conditions, which implies a cost reduction and a better quality of the final effluent (de Lemos Chernicharo, 2007).

The most common treatment strategy for the industrial control of wastewater treatment systems is the measurement of water quality parameters in the effluent to check the appropriate working conditions of the processes. Usually these parameters are analysed at certain time intervals, although new advances are focused on real time measurement of the water quality parameters such as pH, TOC, turbidity, conductivity and temperature (Storey et al., 2011).

The monitoring of biological processes can be undertaken by pH, alkalinity, volatile acids concentration and mixed liquor suspended solids measurements (de Lemos Chernicharo, 2007). In addition, transmembrane pressure measurements are usually monitored in order to apply the cleaning protocols in membrane systems.

More sophisticated techniques have been used at industrial scale, due to its possibility to real on-line monitoring of processes, such as the focussed beam reflectance measurement (FBRM) technique, for the optimization and control of flocculation processes (Negro et al., 2005). FBRM reports particle size distributions in real time without sample manipulation and without measurement process interference of the treatment (Blanco et al., 2002a; 2002b).

Other existing technologies to improve the control of the wastewater treatments include on-line ultraviolet - visible (UV-vis) spectroscopy. The automated system of gas chromatography – mass spectroscopy (GC–MS), liquid chromatography – mass spectroscopy (LC–MS), and high performance liquid chromatography (HPLC) provide reliable information on micropollutants, particularly in water intake monitoring, in near to real time (Storey et al., 2011). Finally, membrane induction mass spectroscopy (MIMS) technique has achieved the on-line monitoring of volatile organic pollutants formed in AOPs; however other compounds, such as the ones formed during phenol oxidation, cannot be monitored efficiently (Nogueira et al., 1999).

However, AOPs optimization and control is based on the measurement of some water quality parameters at pre-selected time intervals. COD, TOC, BOD and redox potential are some of the parameters most often measured. In addition, several techniques have been used to characterize organic compounds sequence during oxidative treatment, among them HPLC (Dzengel et al., 1999; Vinodgopal and Peller, 2003; Wang and Wang, 2008), GC-MS (Justino et al., 2010; Poerschmann and Trommler, 2009), Fourier transformed infrared spectroscopy (FTIR) (Abbas et al., 2008; Araña et al., 2001) and several combinations between them or with other analytic techniques such as UV-vis, LC-MS or ion chromatography (IC) (Carlos et al., 2008; 2009; Devi et al., 2009; Kayan et al., 2010; Udrea and Bradu, 2003). FTIR has been applied to solid samples in order to study catalyst's surfaces and adsorbed substances during AOPs (Araujo et al., 2005; Horikoshi et al., 2008; Palmisano et al., 1994; Sayed, 2004). Gaseous samples have also been analysed using the FTIR technique in ozonation processes measuring CO_2, understandable as mineralized carbon in the outlet gas stream, as an indirect control parameter of the reaction (Carr and Baird, 2000). This technique has been used for reaction control by identifying compounds via the periodic sampling of the liquids (Abbas et al., 2008; Araña et al., 2001). All these methods imply a greater measurement time, whereas on-line information of AOPs to achieve the complete characterization of compounds produced during the reaction is not available.

Moreover, for the real on-line control of AOPs applied at industrial scale it would be useful to develop an easy methodology and technique. The on-line information would allow a better understanding of the reaction mechanisms, as well as an accurate optimization of the reagents doses and reaction time, which will reduce the

associated costs. Recently, an on-line FTIR probe has been developed by Mettler Toledo to study chemical reactions and, in this PhD thesis, its application to study and to optimize AOPs has been performed for the first time.

2 OBJECTIVES OF THE RESEARCH

Although the progressive and continuous process improvements during the last decades have resulted in a very high decrease of water consumption in pulp and paper industry, the current water stress in some regions, like Spain, force industry towards a further closure of the water circuits. This closure is critical due to the exponential accumulation of contaminants and it requires the implementation of advanced treatments to avoid any effect on the production capacity or the paper quality (Gavrilescu et al., 2008). Pollutants must be removed by specific treatments to avoid deterioration in process water quality and to minimize the environmental impact of final effluents.

Biological treatments are not able to remove recalcitrant compounds from wastewaters; as a consequence, other processes such as advanced oxidation must be incorporated into the treatment system. These processes can be applied to process waters or final effluents as an additional advanced treatment integrated into the conventional physico-chemical and/or biological processes, thus increasing the overall efficiency of the treatment.

In addition, the pollutants accumulated in pulp and paper mill effluents depend on the product, the process and the raw material used in the mill. Therefore, the treatment processes that must be applied depend on the characteristics of the wastewater. Before the selection of the optimum treatment train, appropriate combinations must be developed and validated to avoid unnecessary costs. On the other hand, if AOPs are used, the influence of common substances present in pulp and paper mills wastewaters, such as carbonates that can act as scavengers of the AOPs reducing their oxidation efficiency, must be assessed. Finally, new on-line methodologies need to be developed to improve the control of the oxidation reactions, to find out the degradation pathways for target pollutants and to optimize the treatment conditions, depending on the final purpose of the treatment.

Figure 7 shows the combination of treatments evaluated in this doctoral thesis for both pulp and paper effluents. In addition, it shows the synthetic waters used for studying the effect of scavengers in AOPs, lignin synthetic solution, for developing the on-line FTIR methodology and for studying the degradation mechanism of target compounds, phenol and 1,4-dioxane.

In summary, the global objective of this PhD thesis is to generate new knowledge on the applicability of AOPs to help papermakers to further reduce the pollution load of pulp and paper industry wastewaters. The optimization of the water treatments will improve the process water quality and will reduce the pollutant load of the final effluents.

In order to achieve this main objective, the followed specific objectives have been defined:

1. To identify the current limitations described in the state of the art of the AOPs applied to effluents of pulp and paper industry (**PAPER I**).
2. To validate technically the treatment of kraft pulp mill effluents by AOPs in order to reduce the pollutant load and to increase the water biodegradability to increase the efficiency of the biological treatments and thus minimize the load of the final effluent (**PAPER II**).
3. To establish the best treatment train combining AOPs and biological processes to achieve the reclamation of a newsprint recycled paper mill

effluent reaching the quality requirements to be reused in the process in order to further close the water circuit (**PAPER II**).

4. To develop treatment alternatives to remove recalcitrant matter from retentate streams (**PAPER III**).

5. To establish the influence of alkalinity on photocatalyzed processes and on their catalysts behaviour (**PAPER IV**).

6. To develop a new methodology to control AOPs, using an on-line FTIR probe. To validate the FTIR methodology using a model compound very well known, phenol. To apply this new methodology to real wastewaters from pulp and paper industry and to a target compound, 1,4-dioxane, in order to accurately remove recalcitrant matter, increase biodegradability and contribute to clarify 1,4-dioxane degradation mechanism (**PAPER V and VI**).

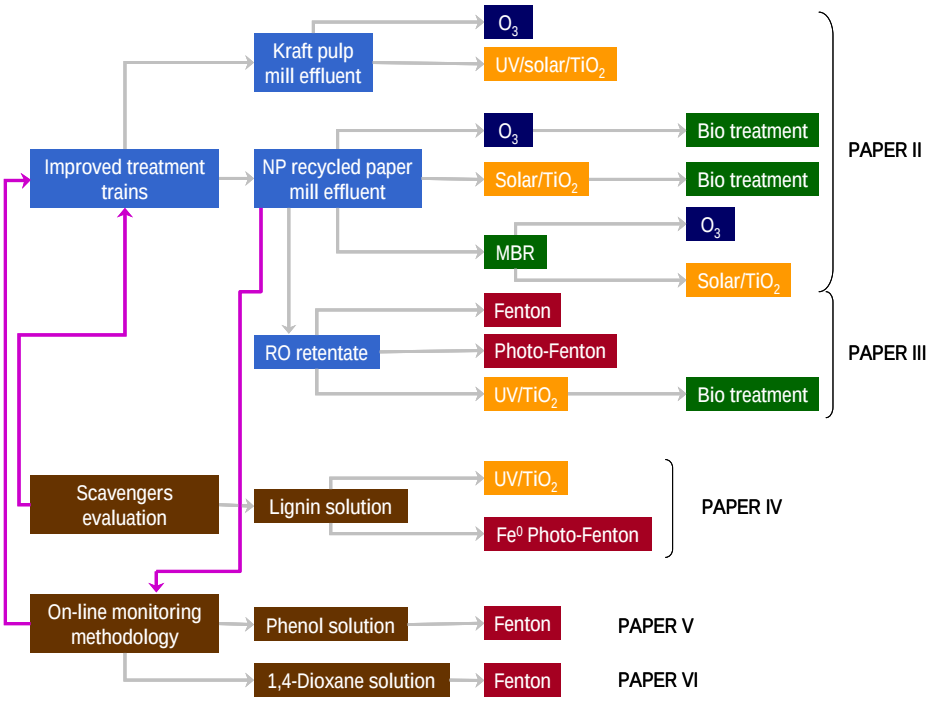

Figure 7. Water treatment trains studied for achieving the global objective of this thesis.

3 METHODOLOGY

3.1. Water samples

Water samples were taken from a kraft pulp mill placed in Biscay, Basque Country and from a recycled paper mill placed in Madrid. The kraft pulp mill was chosen because of the low biodegradability and high toxicity of the effluent and its need for an adapted solution to its small size to minimize the environmental impact of the effluent. In this case, the AOPs were chosen as alternative treatment to increase the biodegradability of the wastewaters, allowing an increase of the efficiency of a post-biological treatment.

The recycled paper mill uses 100% recovered paper to produce newsprint. This type of mills cannot work with a total closure of the water circuits due to the high

quality requirements of the process water. This particular mill was selected because it is a reference in Europe in water management with a very low water consumption (<8 $m^3 t^{-1}$); therefore, the reclamation of the effluent is the next step that must be performed to further reduce fresh water consumption. As a consequence, combinations of biological treatments, particularly MBR, and AOPs were chosen to reclaim this effluent.

On the other hand, previous studies have shown that a RO treatment could be technically viable to reuse the effluent if silica is successfully removed and RO retentates are treated before its discharge to avoid that the final effluent exceeds the limits to accomplish the current legislation. Therefore, the RO retentate from the last treatment step of a pilot plant installed in the recycled paper mill was taken and treated by AOPs. The pilot plant (Figure 8) combined biological and membrane filtration technologies to treat the wastewater flowing out from a DAF unit placed in the first water loop of the deinking plant, which is the most contaminated stream of the recycled paper mill. This pilot trial was performed to assess the feasibility of reclaiming the paper mill effluent in order to reuse it within the process.

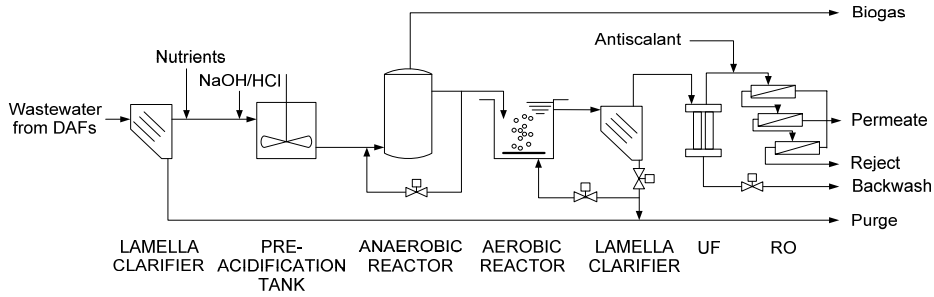

Figure 8. Flow diagram of the pilot plant (Ordoñez et al., 2010).

In all cases, the preservation of the samples, the analyses and the measurements described below were performed according to the standard methods for the examination of water and wastewaters (APHA et al., 2005). A general description of the analyses and protocols carried out to study the efficiency of AOPs is shown in Figure 9. Probes for pH, conductivity, redox potential and dissolved oxygen (ProODO, YSI Inc., Ohio, USA) were used for the on-line control of the reactions. Temperature was kept constant using a thermostatic bath (Model FL300, JULABO Labortechnik GmbH, Seelbach, Germany) when required.

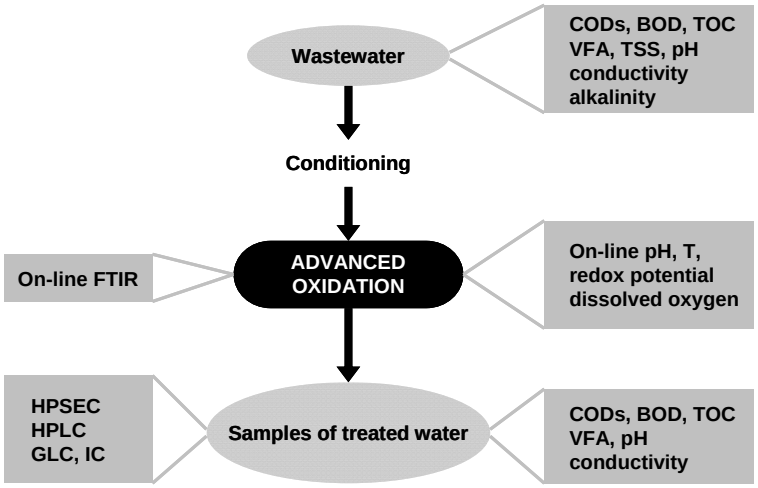

Figure 9. Schematic representation of the general analyses performed in the AOPs experiments.

3.2. Analytical techniques

Soluble chemical oxygen demand (CODs) was measured by the colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermos Scientific AQA 091801, Waltham, USA). H_2O_2 concentration was analysed using the titanium-sulphate spectrophotometric method (Pobiner, 1961). As residual H_2O_2 in the solution interferes with CODs analysis, this interference was corrected if required by fitting the relationship between CODs and H_2O_2 content to a second order polynomial equation (equation 1) (Hermosilla et al., 2009a).

$$CODs_{H2O2} = -0.000020 \cdot [H_2O_2]^2 + 0.393239 \cdot [H_2O_2] \; R^2 = 99.92\% \; p = 0.0001 \qquad \text{(eq 1)}$$

Total organic carbon (TOC) was measured by the combustion-infrared method using a TOC/TN analyser multi N/C® 3100 (Analytik Jena AG, Jena, Germany) with catalytic oxidation on cerium oxide at 850 ºC.

Colour was measured using the Pt-Co method, turbidity was measured with the nephelometric method and volatile fatty acids (VFA) were measured using a colorimetric method described by Harwood and Huyser (Harwood and Huyser, 1968). BOD_5 was measured using a selective electrode; alkalinity was measured by

titration and the mixed liquor through filtration and drying. Finally, total nitrogen and phosphates were measured by colorimetric methods.

3.2.1. High-performance size exclusion chromatography

Lignin and its degradation products were studied in section 5 "Scavengers in photocatalysed AOPs" in order to monitor the degradation of the lignin and to establish the influence of scavengers on lignin degradation. That was performed by the measurement of periodic samples, using high performance size exclusion chromatography (HPSEC). HPSEC was carried out using an HPLC (Shimadzu VP Series, Shimadzu, Milton Keynes, UK) with UV detection set to 254 nm. The mobile phase was 0.01 M sodium acetate at a flow rate of 1 ml·min^{-1}. The column was a TSK – gel G3000SW 7.5 mm (ID) × 30 cm and the guard column was TSK gel 7.5 mm (ID) × 7.5 cm (Tosoh BiosepGmbH, Stuttgart, Germany). For each sample a chromatogram of UV absorbance (arbitrary units) against time (minutes) was produced. The measurement of the molecular weight in the solution allows the identification of the breakage of the organic polymers into smaller molecules even if they have the same structural characteristics.

3.2.2. Focus beam reflectance measurement

Behaviour of the TiO_2 and Fe^0 catalysts in section 5 "Scavengers in photocatalysed AOPs" was assessed with a M500L FBRM probe manufactured by Lasentec (Mettler Toledo, Seattle, WA). The FBRM instrument operates by scanning a highly focussed laser beam at a homogeneous suspension, reporting an on-line measurement of the chord length distribution without any interference of the method on the process studied. The measurement is based on the time duration of the backscattered light from these particles. The temporal duration of the reflection from each particle multiplied by the velocity of the scanning laser results in a characteristic measurement of the particle geometry, namely chord length. Each particle detected is counted and thousands of chord length measurements are collected per second, producing a histogram in which the number of observed counts is sorted into several chord length bins over the range 0.5 to 1000, or 2000 μm (Blanco et al., 2002a). These data give information about the aggregation of the catalyst under different conditions, which will affect the process efficiency.

3.2.3. FTIR equipment

ReactIR iC10 (Mettler-Toledo, Columbia, USA) is a real-time *in situ* reaction monitoring system developed for "the needs of organic and process chemists in

Process Research and Development labs" and it has been applied for the first time in wastewater treatments for improving knowledge about AOPs reactions and mechanisms (section 6 "New monitoring tools for AOPs"). It is based on FTIR spectrometry that is able to provide all the organic chemical species that are present in the solution as the reaction is performed over time. The FTIR spectrometer (Figure 10) uses a mercury-cadmium telluride (MCT) detector that is cooled by liquid nitrogen. Measurements are taken optically using a diamond-tipped probe with a 1 metre long fibre-optic conduit. This system was purged using instrumental-grade air; therefore preventing water vapour from collecting inside the optics, which may otherwise obscure spectral data.

Figure 10. On-line FTIR technique.

Data acquisition was performed from 2000 to 650 cm^{-1} with an 8 cm^{-1} nominal resolution. 256 scans were co-added for each spectrum. A background of pure water was carried out using the same resolution and scanning conditions of the trials before each spectral record. These water spectra were subtracted from the corresponding resulting on-line spectra.

Real-time component analyses were performed using ConcIRT software (Mettler-Toledo, Columbia, USA), which applies the curve-resolution mathematical algorithm for grouping wavenumber values that change absorbance intensity in the same way. This software calculates the associated component spectrum and the relative concentration profile in terms of absorbance units for each group. Furthermore, it re-analyses and updates all spectra and concentration profiles as each new reaction

spectrum is acquired. In short, calculation results evolve as the reaction proceeds, and every organic component (reagent, intermediate or product) that is present in the solution is detected in real-time; and its relative concentration profile is therefore provided.

This equipment has been used for the control of Fenton reaction treating synthetic wastewaters in order to develop an on-line methodology for its use with industrial wastewaters and to assess their degradation mechanisms improving our knowledge about the process, as described in section 6.1 “Development of on-line FTIR methodology to monitor the Fenton process”.

3.2.4. High-performance liquid chromatography

Phenol and its relevant reaction intermediates (hydroquinone, benzoquinone, catechol, acetic acid and oxalic acid) studied in section 6 “New monitoring tools for AOPs” were measured by HPLC (Model L920, Varian, CA, USA) with diode array (PDA) detection to check the presence of some degradation products of phenol and to validate the on-line FTIR results. Acetonitrile - water with the following proportions: 15%:85% and 50%:50% were used as the eluent for aromatics and carboxylic acids, respectively. Sample injections of 20 µL were separated on a C-18 column (Vidac 250 mm x 4.6 mm ID x 5µm) at 30 ºC. The target compounds were measured at the following wavelengths: hydroquinone (290 nm), benzoquinone (245 nm), catechol (280 nm), phenol (270 nm), acetic acid and oxalic acid (200 nm).

3.2.5. Gas-liquid chromatography

1,4-dioxane and an intermediate degradation product (ethylene glycol) used in section 6 “New monitoring tools for AOPs” were identified and quantified by gas–liquid chromatography (GLC) on a 7980A instrument (Agilent Technologies Inc., Palo Alto, CA) equipped with a flame ionization detector. Injector and detector were respectively set up at 310 and 280°C. Samples (2 µL) were injected using the *pulsed-split* mode (*split* ratio 5:1) and analysed in a TRB-FFAP (Teknokroma, Sant Cugat del Vallès, Spain) fused silica column (30 m × 0.25 mm internal diameter × 0.25 µm film thickness), with He (43 psi) as the carrier gas and a temperature programme (80°C to 240°C, 9 minutes initial hold, 15°C·min^{-1} ramp rate). Peaks were identified on the basis of sample coincidence with relative retention times of commercial standards. Quantification was performed according to peak area, corrected with the response factors calculated for each compound using 1-butanol (250 ppm) as the internal standard and the software *GC-ChemStation Rev.B.04.02 (96)* from Agilent.

3.2.6. Ion chromatography

Ion chromatography (IC) was used to identify the formation of some possible by-products (formic, oxalic, acetic, glycolic, and methoxyacetic acids) during the degradation of 1,4-dioxane in section 6 “New monitoring tools for AOPs”. They were complementarily identified and quantified by IC using a Dionex DX-500 device (Thermo Scientific, Sunnyvale, CA) equipped with a conductivity detector. A 40 to 60 mM NaOH gradient was used as the eluent for measurement keeping the flow at 1.5 $L{\cdot}min^{-1}$. The injection loop was 75 L. An AS11HC Ion Pac ionic resin column was used aided with a previous Anion Trap Column (ATC3) and an AG11-HC guard column. Peaks were identified and quantified on the basis of sample coincidence to relative retention times and standard concentrations of commercial standards.

3.3. Experimental procedures

3.3.1. Ozonation treatment

Ozonation trials were performed in a glass jacketed cylindrical bubble reactor (height = 1 m, diameter = 5 cm) with a continuous feed of ozone gas (4.0 $L{\cdot}min^{-1}$) produced from ordinary grade air passed through polycarbonate filters, and subsequently enriched with oxygen (Figure 11). The system consisted of an ozone generator (Model 6020, Rilize, Gijón, Spain), and a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The Netherlands). As a result, 3 $g{\cdot}h^{-1}$ of ozone were continuously fed into the reactor. The real ozone consumption inside the reactor was determined by in-flow and out-flow ozone concentrations using two on-line ozone analysers (Model 964C, BMT Messtechnik GMBH, Berlin, Germany). Unconsumed ozone was sent to a catalytic ozone destructor. A peristaltic pump (Masterflex® Console Drive, Cole-Parmer Instrument Company, Illinois, USA) was used to recirculate the solution under treatment through the reactor.

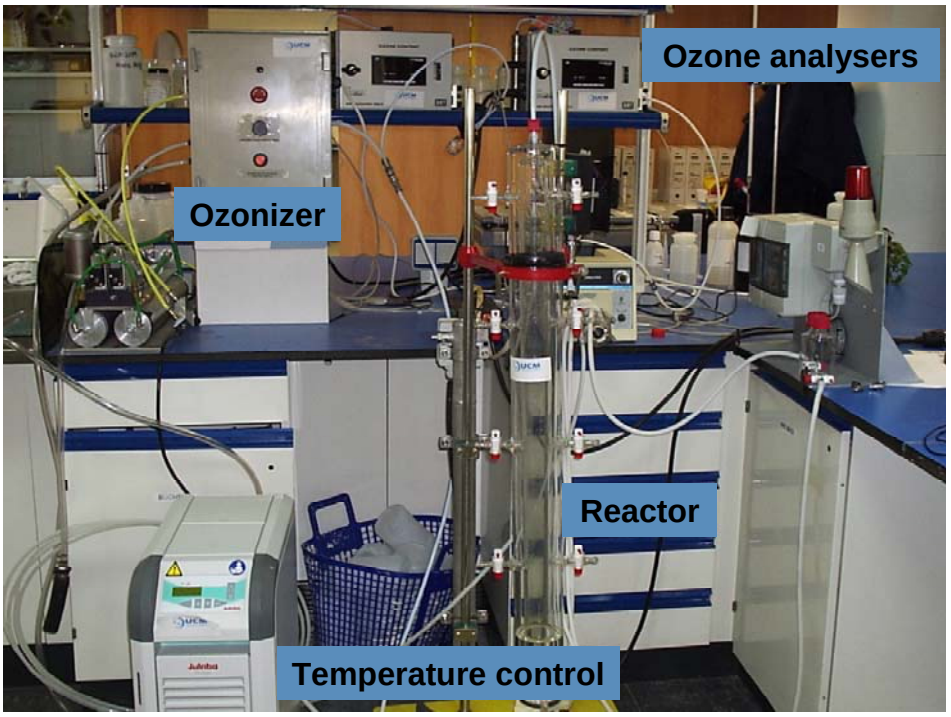

Figure 11. Equipment for the ozonation treatment

3.3.2. TiO_2 photocalysis treatment

The solution to be treated was kept mixed along the process using a magnetic device. If required, pH adjustment and control by 1N H_2SO_4 and 1N NaOH was made. Then, TiO_2 (AEROXIDE® TIO_2 P 25, Evonik Degussa GmbH, Essen, Germany; BET surface area = 50 $m^2 \cdot g^{-1}$; pore volume = 0.25 $m^3 \cdot g^{-1}$, and mean particle size of ca. 30 nm) was added. Subsequently the UV-lamp was switched on. The samples were centrifuged for 15 minutes at 335 g and/or filtrated through 0.45 μm syringe filters. Among the UV sources, several lamps were used during the research.

450-W high-pressure mercury immersion lamp

The photocatalytic and photo-Fenton processes studied in section 4 "AOPs applied to pulp and paper mill wastewaters" were performed in a reactor with a 450-W high-pressure mercury immersion lamp from ACE-glass (Vineland, USA). This lamp

was enclosed inside a quartz glass vessel through which water was circulated to reduce the excessive heat generated during UV irradiation, and it was vertically located in the centre of the reactor. The entire assembly was kept inside a photochemical safety cabinet.

The total radiated power of the 450-W lamp, in the visible and UV regions, was 159.4 W (47.5% and 52.5%, respectively). A total photon flux of $1.1 \cdot 10^{20}$ photon·s^{-1} was calculated to flow inside the photochemical reactor as described by Liang et al. (2011).

Light intensity was recorded using a radiometer (UV-Elektronik, UV-VIS Radiometer RM-21, Ettlingen, Germany), resulting in 1860 W·m^{-2} between 315 to 400 nm at the mid-height of the 450-W UV-lamp and at 1.5 cm from the light source, which was the distance between the sample and the irradiation source.

Solar simulator

Solar photocatalysis trials, presented in section 4 "AOPs applied to pulp and paper mill wastewaters", were carried out in a solar simulator equipped with a Xenon lamp (300 W) supplied by Newport (Irvine, USA). The intensity and power could be pre-selected for each experimental run, and a filter was used to correct the illuminator in order to obtain a solar spectrum under ideal conditions (ASTM E490-73a).

The total radiated power of the solar simulator was 106.5 W (51.7% in the visible region and 48.3% in the UV region). A total photon flux of $6.8 \cdot 10^{19}$ photon·s^{-1} was calculated for the solar simulator as described by Liang et al. (2011).

Light intensity was recorded using a radiometer (UV-Elektronik, UV-VIS Radiometer RM-21, Ettlingen, Germany), resulting in 989 W·m^{-2} between 315 to 400 nm at the mid-surface of the Xe lamp and at 12 cm from the light source, which was the distance between the sample and the lamp.

Collimated beam apparatus

UV experiments in section 5 "Scavengers in photocatalysed AOPs" were conducted in a Wedeco AG bench scale quasi-collimated beam apparatus (Herford, Germany) fitted with four 30 W low pressure Hg lamps that emit monochromatic light at 254 nm. A warm up time of 30 minutes was allowed to ensure consistent light output before irradiating the solution. UV irradiance from the collimated beam was determined to be 22.6 W·m^{-2} using the uridine actinometry method as described by von Sonntag and Schuchmann (1992).

3.3.3. Fenton processes

The solution under treatment was mixed with a magnetic device during the process. After an initial pH adjustment, when required, Fe^{2+} as ferrous sulphate (Fe_2SO_4) or Fe^0 was added in order to reach the iron concentration wanted. H_2O_2 was then added until the desired concentration was reached. Aliquots of treated solution were periodically sampled with a syringe thereafter. These samples were neutralized to pH ≈ 9.00 by adding 40% sodium hydroxide. They were then centrifuged for 15 min at 335 g or directly filtered through 0.45 μm syringe filters. Treatments were usually run until H_2O_2 had been fully consumed.

The UV-assisted Fenton treatment was performed following the same experimental procedure plus a source of UV light assisting the Fenton process.

3.3.4. Biodegradability test

Zahn-Wellens/EMPA Test (EPA, 1998) was used to determine the inherent biodegradability of the solutions. 7-days-old activated sludge was collected from the wastewater treatment plant located in the recycled paper mill. This biodegradation process was monitored measuring CODs in filtered subsamples until its maximum reduction was achieved. The functional power of the activated sludge was checked by running a parallel test using ethylene glycol as the reference substance, whose biodegradability achieved at least a 70% CODs reduction within 14 days of incubation. The ratio of the removed CODs to its initial value, corrected taking into account the control results, provides the percentage of biodegradation being achieved along the process.

3.3.5. Membrane bioreactor technology

The MBR pilot system used during the combined treatment trials, presented in section 4 “AOPs applied to pulp and paper mill wastewaters”, was a ZeeWeed-10 from Zenon (GE; Conneticut, USA) with an outside/in ultrafiltration hollow fibre membrane (Figure 12). The used membrane module had a mean pore size of 0.04 μm, and an effective filtration area of 0.93 m^2. The system assembled two process tanks summing up a total effective volume of 70 L. Wastewater was pumped through the membrane by developing a negative pressure (vacuum) with the use of a gear pump (Verder VGS060.17, maximum 60 $L{\cdot}h^{-1}$) regulated by a frequency controller.

The MBR started up with 70 L of returned activated sludge collected from the wastewater treatment plant installed in the recycled paper mill, and it was fed with

wastewater from this mill after sedimentation. In terms of operation, the process consisted of 300 s of direct filtration and 20 s of backwash. Solids were filtered out via direct filtration.

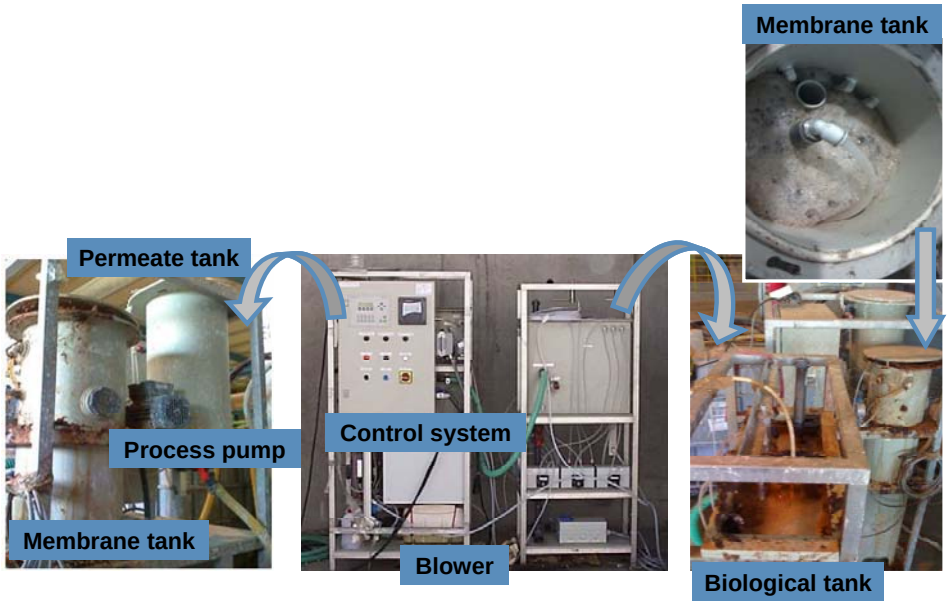

Figure 12. MBR pilot system from General Electric.

4 AOPs APPLIED TO PULP AND PAPER MILL WASTEWATERS

The main objective of this section, corresponding to papers II and III, was to reduce the pollution of the pulp and paper mill effluents through the study of the best treatment trains, applying advanced oxidation processes. The achievement of this objective will produce an improvement of effluent quality and numerous associated environmental benefits as well as a significant reduction of water consumption if the treatment chain to reclaim the effluent is totally validated.

With the purpose of covering the most critical cases, three wastewaters from the pulp and paper industry were assessed. The studied wastewaters were a kraft pulp mill effluent, a recycled paper mill effluent and a RO retentate. In order to establish the best treatment strategy for each wastewater, AOPs were applied, and

combinations with biological treatments were checked if needed to enhance overall treatment efficiency with a cost reduction.

4.1. Wastewater 1: kraft pulp mill effluent

The characterization of this effluent was obtained over six months of sampling. The main analytical characteristics are detailed in Table 3. These wastewaters are usually poorly biodegradable as they are characterized by the presence of toxic and bio-recalcitrant compounds. As a consequence, pre-treatments are needed to ensure a high efficiency in a biological treatment.

Table 3. Initial characteristics of the sampled kraft pulp mill effluent.

	Average	Standard deviation
CODt, $mgO_2 \cdot L^{-1}$	1749	435
CODs, $mgO_2 \cdot L^{-1}$	1532	328
BOD_5, $mgO_2 \cdot L^{-1}$	850	370
VFA, $mg \cdot L^{-1}$	285	54
Conductivity, $\mu S \cdot cm^{-1}$	3553	255
Alkalinity, mg $CaCO_3 \cdot L^{-1}$	83	3
TSS, $mg \cdot L^{-1}$	314	123
pH	5	1.1

In order to increase the biodegradability and to reduce pollutant load of the water, several AOPs have been evaluated: ozonation, UV and solar TiO_2 photocatalysis were applied independently to the kraft pulp mill effluent. Experiments were performed in triplicate. Ozone treatment of 1.5 L of solution was performed at pH 7 and 12 in order to optimize the ozone dose. The concentration of TiO_2 and the time of reaction were optimized at pH values of 7 and 12 with a 450 W

UV lamp treating 2 L of solution and 1.25 L at pH = 7 using the solar simulator keeping T = 25 ºC. The CODs was measured after filtrating samples through 0.45 μm. Each ozonation or photocatalysis trial was performed for 5 hours; and samples were taken every hour for CODs, colour, and VFA determination.

4.1.1. Results and discussion

4.1.1.1. Ozone treatment

The evolution of ozone consumption presented different results over the course of the treatment because of the continuous reaction of ozone with the changing organic and inorganic compounds present in the solution. This treatment resulted in a significantly higher CODs reduction at an initial pH = 7 than at pH = 12 (Figure 13), although several authors have reported higher effectiveness at basic pH (Amat et al., 2004; 2005b; Bijan and Mohseni, 2004; Sevimli, 2005; Wang et al., 2004). Higher pH values accelerate ozone decomposition forming OH· (Barndok et al., 2012) that are expected to be more efficient. However, results showed that the current effluents would be most suited to their oxidation treatment at their common neutral pH value, probably due to direct oxidation by ozone. Direct ozone oxidation is more selective oxidizing specific pollutants in the wastewaters than OH·, which can be scavenged by the high alkalinity at higher pH values. Moreover, working at the pH value of the wastewaters can avoid the cost of pH control operations at industrial scale.

The ozone treatment of these effluents was performed through consecutive oxidation stages (Figure 13), and each stage involved different ozone dosage consumption depending on the organic load of the effluent and its initial pH. Two main reaction stages could be differentiated: (1) the oxidation of the easily oxidizable compounds which happened first; and (2) the degradation of oxi-recalcitrant by-products that are formed along the process (Fontanier et al., 2005; Salokannel et al., 2007).

These successive oxidation stages happen during all the reaction; and although there is a steep removal of the CODs at the beginning of the process due to the effective oxidation of oxidable products (1 $g{\cdot}L^{-1}$ O_3 as shown in Figure 13), the CODs removal increases slowly thereafter due to the higher oxi-recalcitrant by-products accumulation as they are not removed (Hermosilla et al., 2009a); consequently the dosage of ozone increased. In fact, the limitation of TOC abatement is one of the results of the progressive accumulation of oxi-recalcitrant by-products in the solution (Hoigne and Bader, 1983); although they are generally characterized for being highly biodegradable.

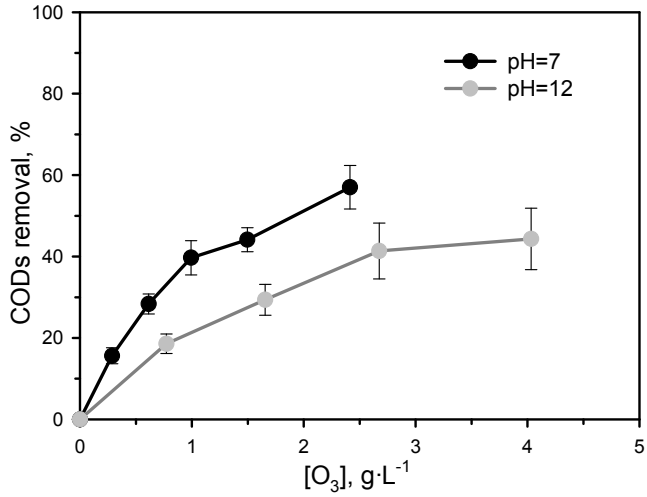

Figure 13. CODs reduction obtained over the ozonation treatment of the effluent from a kraft pulp mill.

At pH = 7, a first stage of good oxidation efficiency prevails until 1.2 $g{\cdot}L^{-1}$ of O_3 were consumed. The ratio of consumed O_3 to removed CODs was 1.6 along this first oxidation stage; that is, this effluent clearly showed a higher content of those compounds that may be easily oxidized by ozonation at this point, so this oxidation stage lasted longer. On the other hand, at pH = 12, oxidizable by-products were degraded with a ratio of supplied O_3 / removed CODs of 1.9 until 0.8 $g{\cdot}L^{-1}$ of O_3 were consumed. Further oxidation implied a much higher ratio of consumed O_3 / removed CODs of 15 between 0.8 and 4.0 $g{\cdot}L^{-1}$ of supplied O_3, most likely because of the greater accumulation of oxi-recalcitrant compounds in the solution. In short, a higher ozone dose was required at pH = 12 for obtaining the same CODs removal than at pH = 7 because higher pH values may accelerate ozone decomposition (Barndok et al., 2012) which decreased the CODs removal in these particular wastewaters that had a greater reactivity with molecular ozone.

4.1.1.2. TiO_2 photocatalysis treatment

The maximum reduction of the CODs that was achieved by photocatalysis turned out to be lower than the figures reported for the ozonation (Figures 13-14). This lower removals are in accordance with the previous reports (Amat et al., 1999;

2005b; Fontanier et al., 2005; Miranda et al., 2001; Perez et al., 2001) whether using a UV light or assisting the process with a solar simulator (Figure 14).

Although degradation results showed the same tendency whichever light source was used, reduction of CODs resulted slightly higher (<5%) when the solar simulator was assisting the photocatalytic process, particularly when tested at the higher TiO_2 concentration level (10 $gTiO_2 \cdot L^{-1}$; Figure 14). This detail may ultimately be explained in terms of differential properties of the incident light, and other characteristics of the reactors used that might have somehow changed the distribution and efficiency of the suspended catalyst. In this case, using the sun as a light source would at least result in reduced energy costs of the treatment without causing any efficiency loss.

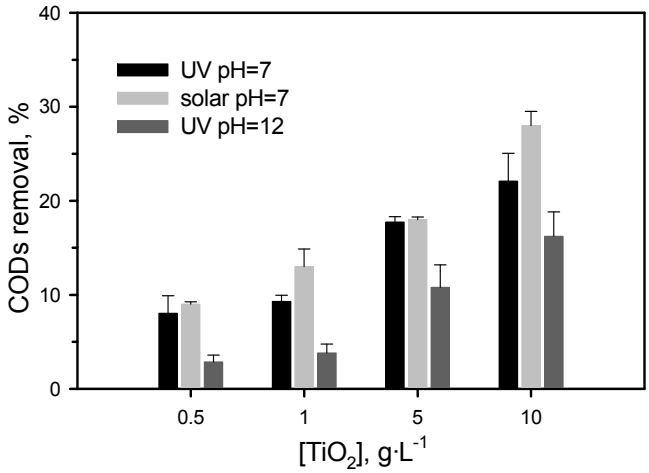

Figure 14. Influence of [TiO_2], pH and source of light on the photocatalytic treatment of kraft pulp mill effluent.

As expected, the efficiency was greatly influenced by the dosage of TiO_2 (Figure 14). There was higher degradation of organic matter when the TiO_2 concentration was also higher (up to 10 g $TiO_2 \cdot L^{-1}$) regardless of the light source and initial pH value used. These results are in accordance with those reported by Chang et al. (2004) for a similar treatment of synthetic water of lignin powder.

Although several authors have reported good reductions of organic compounds by photocatalytic treatments of biologically pre-treated pulp effluents at both neutral and basic initial pH values (Catalkaya and Kargi, 2008; Peralta-Zamora et al., 1998;

Perez et al., 2001), the fact is that the reduction of the CODs was higher when UV photocatalysis was performed at pH = 7 rather than at 12 (Figure 14). This may partially have been caused by the varying degrees of competition that anions, cations, and some neutral molecules exert against organic contaminants for the reactive sites on the surface of TiO_2 particles. The reaction rate would be slowed down by anion adsorption on the surface of the positively charged catalyst under acidic conditions; whereas catalytic particles are negatively charged under basic pH values, and the presence of cations may therefore affect the reaction rate.

4.2. Wastewater 2: recycled paper mill effluent

Effluents from paper mills using recovered paper as raw material are characterized by the presence of more biodegradable products than in the case of kraft pulp mill effluents. The main analytical characteristics of recycled paper mill wastewater sampled along six months and measured twice a week, are shown in Table 4.

Table 4. Initial characteristics of the recycled paper mill effluent.

	Average	Standard deviation
CODt, $mgO_2 \cdot L^{-1}$	2319	618
CODs, $mgO_2 \cdot L^{-1}$	2031	459
BOD_5, $mgO_2 \cdot L^{-1}$	959	394
VFA, $mg \cdot L^{-1}$	347	187
Conductivity, $\mu S \cdot cm^{-1}$	2322	396
Alkalinity, mg $CaCO_3 \cdot L^{-1}$	479	184
TSS, $mg \cdot L^{-1}$	344	261
pH	7.8	0.4

The most common treatments for these types of final effluents are primary ones and, depending on the legislation, they can be followed by a biological treatment. However, the final bio-recalcitrant compounds are not easily removed from the effluent. In order to reclaim the effluent, this recalcitrant matter must be removed from the wastewater to avoid its accumulation and to achieve the quality requirements of the process water. The objective of this study is the optimization and assessment of different AOPs in combination with biological treatments, including an MBR, in order to find out the best treatment strategy for this effluent reclamation.

Ozonation, UV and solar TiO_2 photocatalysis and MBR treatments were applied individually or in combination (ozonation or solar photocatalysis + biodegradability test, MBR + ozonation or solar photocatalysis) to assess the synergic effect between the treatments. Ozone treatment of 1.5 L of solution was performed at pH 7 and 12 in order to optimize the ozone dose. The concentration of TiO_2 and the reaction time were optimized at pH values of 7 and 12 with the 450 W UV lamp treating 2 L of solution and 1.25 L at pH = 7 using the solar simulator. Temperature was set at 25 ºC. The CODs was measured after filtrating samples through 0.45 μm. Each ozonation or photocatalysis trial was performed over 5 hours; and samples were taken every hour for CODs, colour, and VFA determination.

During the MBR start-up, sludge drainage was set at 0.4 $L \cdot h^{-1}$ in order to regulate the biomass content inside the MBR. Subsequently, values between 0.4 and 0.9 $L \cdot h^{-1}$ were set to regulate the concentration of solids inside the tanks. The biomass inside the MBR was controlled by measuring the mixed liquor volatile suspended solids (MLVSS) whose average value was 5.92 $g \cdot L^{-1}$. The average sludge age was 16 days at 24 hours of hydraulic retention time (HRT) and 5 days at 8 hours HRT. Total suspended solids (TSS), turbidity, CODs, VFA, mixed liquor suspended solids (MLSS), MLVSS, total nitrogen, and phosphate contents were measured twice a week during the trials.

4.2.1. Results and discussion

4.2.1.1. Ozone treatment

The ozone treatment of the effluent from the recycled paper mill showed a lower reduction of CODs compared to the effluent from the pulp process (section 4.1.1.1.) because it carried higher concentration of compounds that are difficult to oxidize (VFA, mainly), and higher amount of bicarbonate (Table 4), which can produce certain scavenging effects. Aliphatic organic compounds have been widely described to be difficult to oxidize by AOPs (Gogate and Pandit, 2004a; 2004b; Hermosilla et

al., 2009b), resulting in an increase of the consumption of ozone and the consequent decrease of the efficiency of the treatment.

This effluent showed some non-significant differences between the achieved CODs removals at an initial pH = 7 and pH = 12 (Figure 15). When less than 0.5 $g{\cdot}L^{-1}$ of O_3 concentration were consumed, the ratio between the supplied O_3 concentration to the removed CODs was 1.8; whereas it increased to 4 and 5 at pH = 7 and 12, respectively, when the consumed ozone was increased from 0.5 to approximately 1 $g{\cdot}L^{-1}$ due to the dominant presence of oxi-recalcitrant by-products. As a result, the response curve was progressively smoother thereafter (Figure 15).

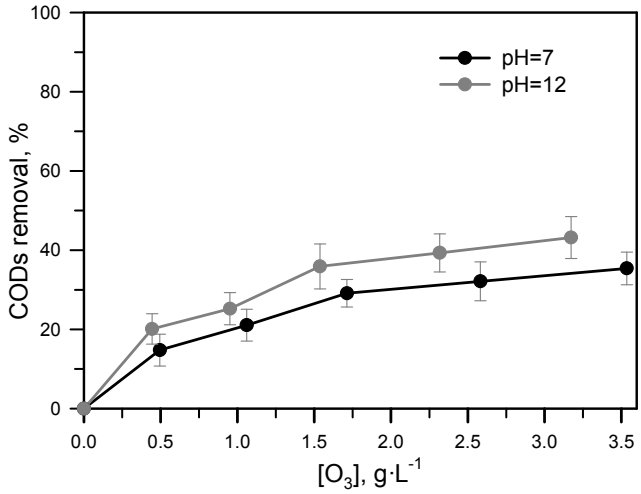

Figure 15. CODs reduction obtained along the ozonation treatment of the effluent from the recycled paper mill.

4.2.1.2. TiO_2 photocatalysis treatment

Photocatalysis treatment of the recycled paper mill effluent reported similar results than the ones of the kraft pulp mill effluent treatment (section 4.1.1.2.), although recycled paper mill effluent showed greater difficulties in its oxidation, achieving lower reductions. As mentioned, this may partially be explained by the higher content of aliphatic organic compounds that are present in the effluent sampled at the paper mill (i.e. VFA content in Tables 3 and 4), which are substances

difficult to oxidize by AOPs (Gogate and Pandit, 2004a; 2004b; Hermosilla et al., 2009b).

UV and solar photocatalysis achieved lower CODs removals than ozone treatment. Slightly higher reduction of CODs was achieved using the solar light at higher TiO_2 dosage (Figure 16). Higher degradation of organics was obtained by increasing the TiO_2 dosage, independent of whether UV or solar light was used. Better results were reported working at pH = 7 than working at pH = 12 with the UV lamp. Therefore, only pH = 7 was tested for the solar simulator. The same conclusions given for the photocatalysis treatment of the kraft pulp mill effluent can be applied in this case.

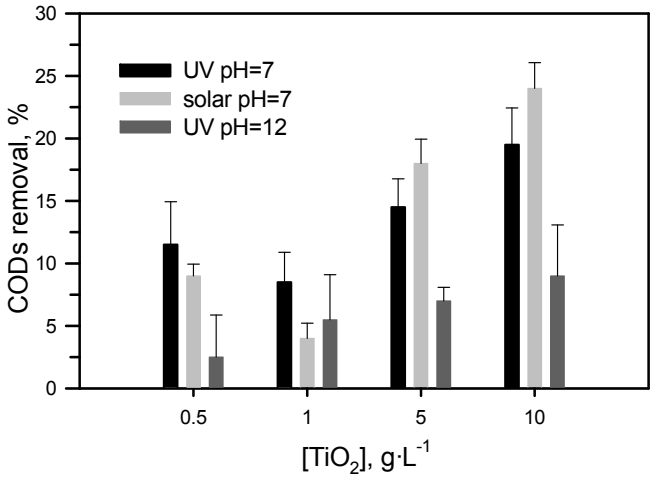

Figure 16. Influence of [TiO_2], pH and light source on the photocatalytic treatment of a recycled paper mill effluent.

4.2.1.3. Combination of AOPs with biological treatment

The oxidation treatment of the effluent from the recycled paper mill showed poor results. Therefore, the combination of AOPs with biological treatment was tested in order to improve CODs reduction efficiency at a lower overall treatment cost. Considering the previously reported capacity of UV and solar photocatalysis to increase the biodegradability of this type of effluent, solar radiation was only assessed, as it showed similar or even better results and the use of solar light as the source for UV radiation is much cheaper.

In a first step, the oxidized wastewater was subjected to a biological degradation through the use of the biodegradability test. Secondly, an initial MBR treatment was applied followed by the oxidation processes (Figure 17). The reaction conditions applied for the oxidation treatments were: 1 $gO_3 \cdot L^{-1}$ at pH = 7 for ozonation; and 5 $gTiO_2 \cdot L^{-1}$ for 30 minutes of solar photocatalysis also performed at pH = 7.

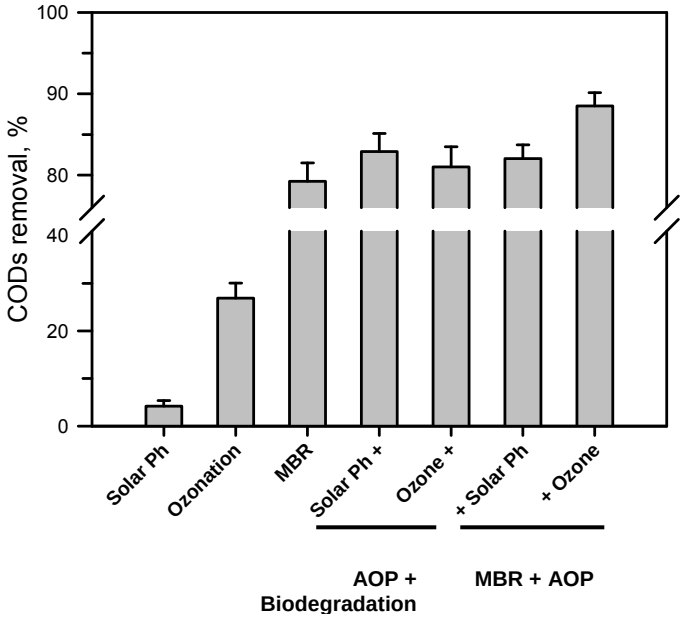

Figure 17. Comparison of solar photocatalysis and ozonation as pre- and post-treatment alternatives of the biological treatments of the effluent from the recycled paper mill. (Ph: TiO_2 photocatalysis)

The MBR was stabilized working with an average of 5-6 $g \cdot L^{-1}$ volatile suspended solids. The average CODs value of this permeate was 250 $mgO_2 \cdot L^{-1}$ when HRT was kept for 24 h (feed/microorganisms (F/M) = 0.44 $kgCODs \cdot kg^{-1}MLSS \cdot d^{-1}$). The sludge age turned out to be 16 days, and sludge retention time (SRT) was about 7.3 days for a 24 h HRT. BOD_5 values of permeate were often lower than 10 $mgO_2 \cdot L^{-1}$. A total or almost complete degradation of biodegradable organic matter was finally achieved by this treatment. In addition, turbidity was on average reduced from 300

to 2 NTU; whereas suspended solids were totally removed. Performing such ozonation or solar photocatalysis pre-treatments of a biological process did not involve much meaningful efficiency improvement (<5%) for this type of wastewater taken from a recycled-paper mill (Figure 17).

The standalone MBR treatment reduced CODs by 80% with almost complete consumption of VFA and a reduction of colour greater than 40% (Figure 18). The remaining 20% of CODs in the permeate is mainly made up of bio-recalcitrant CODs and is therefore adequate for being treated by a post AOP.

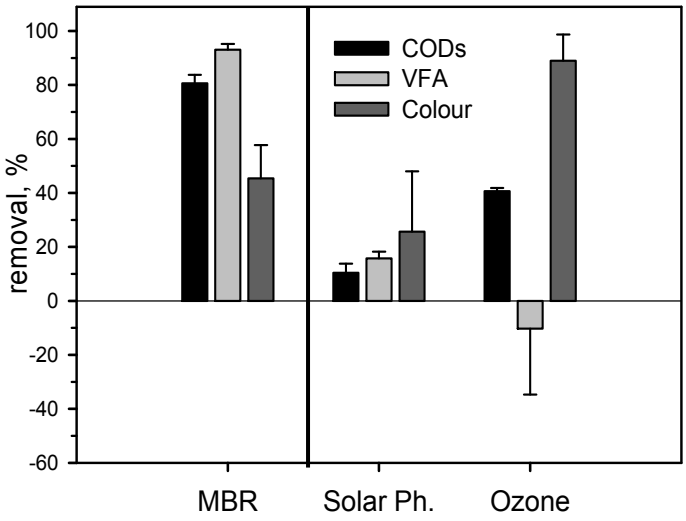

Figure 18. Degradation efficiency results of the MBR biological treatment of the effluent from the recycled paper mill and the oxidation post-treatment of its permeate by solar photocatalysis and ozonation. (Ph.: TiO_2 photocatalysis)

In fact, the ozone oxidation of the MBR's permeate achieved 40% reduction of the remaining CODs (Figure 18); thus enhancing the overall CODs removal significantly by an additional 10% approximately (Figure 17). On the other hand, solar photocatalysis following the biological treatment only achieved 10% removal of the CODs remaining (Figure 18). In addition, ozone was able to almost completely remove the persisting colour in the permeate; as well as producing an increase in the VFA content, thus enabling the recirculation of the ozonised permeate back into

the MBR in order to further increase the efficiency of this treatment strategy. In short, the combination of MBR treatment and ozone oxidation reached 90% overall CODs reduction, and 93% total colour removal. The application of this treatment train to the effluent of newsprint paper mill would allow to significantly reduce fresh water consumption (from 7 to <4 $m^3 \cdot t^{-1}$), keeping CODs values low and displacing the exponential increase of CODs concentration to lower consumption of fresh water (Figure 19).

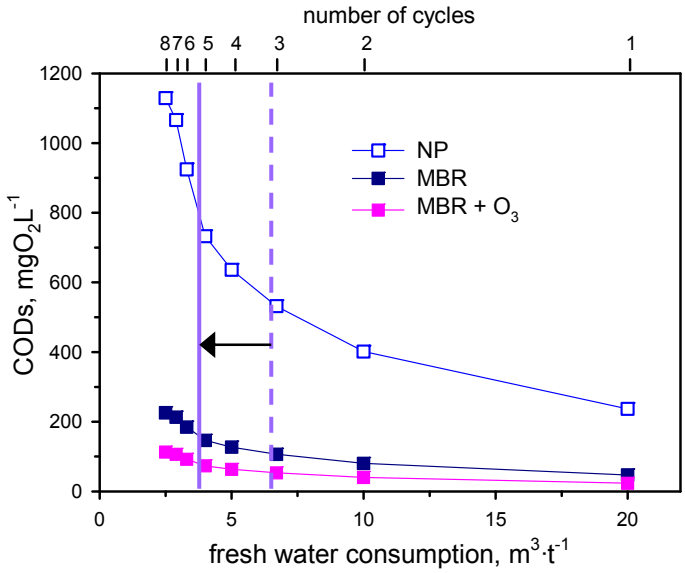

Figure 19. Estimations of dissolved COD accumulated in synthetic newsprint (NP) process water. Estimation of NP wastewater treated by MBR and estimation of NP wastewater treated by MBR+O_3.

4.3. Wastewater 3: RO retentates

In order to achieve zero liquid discharge in this industry, a treatment of the final effluent is mandatory to reuse the effluent as process water. RO with a previous biological and membrane treatment must be included due to the water quality required for being reused in the process (Ordoñez et al., 2010). As a consequence, a retentate stream is obtained during the RO treatment. It is characterized by a high

concentration of bio-recalcitrant pollutants. If this retentate is discharged without treatment, the final effluent will not meet the required quality to be discharge with the minimum cost. Therefore, this section will assess AOPs as an alternative for the treatment of these streams.

Fenton, photo-Fenton and TiO_2 photocatalysis were applied to the RO retentate obtained from a treatment train of the effluent of the recycled paper mill. The sampled RO retentate, whose main analytical characteristics are shown in Table 5, showed the expected load of mid-strength bio-refractory organic and inorganic compounds (Ordoñez et al., 2010).

Table 5. RO retentate characterization.

	Average	Standard deviation
pH	7.5	0.5
T, ºC	23	2
Conductivity, $mS{\cdot}cm^{-1}$	3.7	0.6
CODt, $mgO_2{\cdot}L^{-1}$	530	74
TOC, $mg{\cdot}L^{-1}$	111	13
BOD_5, $mgO_2{\cdot}L^{-1}$	21	4
TSS, $mg{\cdot}L^{-1}$	21	7
Alkalinity, mg $CaCO_3{\cdot}L^{-1}$	750	15

2 L of sample volume were used for all the experiments with RO retentate. Photocatalysis experiments were performed in order to optimize the concentration of TiO_2 and the reaction time whilst maintaining a constant pH (as received, pH = 7.5) and temperature (T ≈ 25ºC). Fenton and photo-Fenton reaction variables were studied using a response surface methodology (RSM) calculated by SYSTAT 13 (SYSTAT Software Inc., Chicago, USA). RSM was performed following a full factorial design considering H_2O_2 concentration levels of 1.0625, 2.125 and 4.250 × initial CODs value ($mg{\cdot}L^{-1}$); $[H_2O_2]_0/[Fe^{2+}]_0$ molar ratios of 1.0, 1.5 and 2.0 for the Fenton

treatment, and up to 30 for the photo-Fenton treatment; and pH values of 2.8, 5.0 and 7.2. It is of particular interest to assess whether shifting closer towards the natural pH value of the treated stream (7.5 ± 0.5; Table 5) may or may not suppose greater treatment efficiency losses.

4.3.1. Results and discussion

4.3.1.1. Conventional Fenton process

pH is one of the main factors limiting the performance of the Fenton treatment of wastewater since it plays a major role in the control of the activity of the oxidant and the substrate, the stability of H_2O_2 itself, and the speciation of iron (Bigda, 1995; Gulsen and Turan, 2004; Hermosilla et al., 2009a; Zhang et al., 2005). As the pH increases, iron precipitates as $Fe(OH)_3$ (Kiwi et al., 1993) and H_2O_2 is decomposed to oxygen (Pulgarin and Kiwi, 1996). However, controlling the pH during the treatment usually implies a higher cost and causes the conductivity of the solution to rise. Therefore, the limit for effluent conductivity set by current environmental legislation may limit its disposal.

The designed RSM identified pH = 2.8 as the optimal value for the Fenton treatment of the sampled RO retentate from the paper mill (Figure 20), which has also been previously reported as the optimal value for the performance of this treatment to landfill leachate (Hermosilla et al., 2009a) and phenol (Kavitha and Palanivelu, 2004). However, it is important to consider the possibility of implementing this process at natural effluent pH values, which is close to neutral (pH ≈ 7.5, Table 5); therefore avoiding the extra cost of controlling the pH, and the potential problems that may be caused by an increase of effluent conductivity. In fact, reasonable reductions of the CODs (60-70%) were achieved working from an initial pH = 7.2, but with a higher dosage of reagents (Figure 20).

The dosage requirements of reagents were properly assessed by RSM in terms of the relative amount of H_2O_2 required per CODs unit, and the molar ratio between H_2O_2 and Fe^{2+} (Figure 20). Results were in good agreement with those previously reported for other wastewaters with high organic load (Hermosilla et al., 2009b; Rivas et al., 2003; Torrades et al., 2011; Zhang et al., 2005). Accordingly, although a 1:1 molar ratio between H_2O_2 and Fe^{2+} corresponds to the theoretical optimal stoichiometry for the formation of $OH\cdot$ in a Fenton reaction (Harber and Weiss, 1934), the better operation conditions were provided by ≈1.5 values regardless of the initial pH value of the reaction, reflecting a net oxidation efficiency loss through parallel reactions (≈33%).

The reduction of the CODs that has been achieved by performing the optimal Fenton treatment of RO retentate from recycled paper mill effluent is higher (>80-

90%; Figure 20) than the best reported for several paper mill effluents (30-85%; (Catalkaya and Kargi, 2007; Sevimli, 2005; Tambosi et al., 2006)). This higher CODs removal is due to the different composition of the retentates compared with paper mill effluents, in which the amount of oxi-recalcitrant compounds that is probably found is higher than that one in RO retentates. Moreover, the removal of LMW compounds in the RO and other previous treatments, such as biological ones, generates an accumulation of HMW compounds in the retentate stream favouring the Fenton process's efficiency.

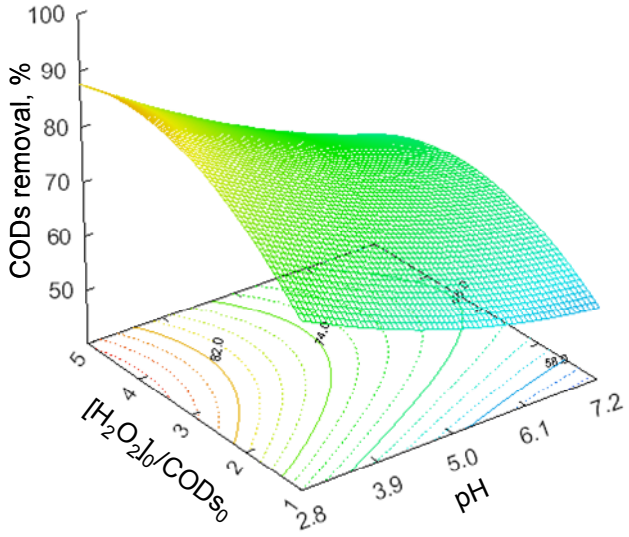

Figure 20. Response surface and contour plot for the removal of CODs from paper mill RO retentate by Fenton treatment considering variable pH and reagents concentrations (T = 25 ºC).

4.3.1.2. Photo-Fenton process

A higher efficiency is possible with photo-Fenton because it enables further treatment of some organic matter that could not be otherwise treated. Furthermore, it also requires much less Fe^{2+}, thus reducing greatly the turbidity and sludge generation (Hermosilla et al., 2009b; Kavitha and Palanivelu, 2004; Kim and Vogelpohl, 1998; Safarzadeh et al., 1997). The progression of the reaction is further

driven by the photo-regeneration of Fe^{2+} from Fe^{3+} and the breakage of iron complexes (Hermosilla et al., 2009b).

In fact, the optimal photo-Fenton treatment of the RO retentate from the paper mill achieved a 100% reduction of the initial CODs (Figure 21). The optimal photo-Fenton reaction conditions were at pH = 2.8, $[H_2O_2]_0/CODs_0$ > 2.25, and $[H_2O_2]_0/[Fe^{2+}]_0$ > 10 (Figure 21). Particularly, the pH turned out to have a greater effect in the applied photo-Fenton process than when performing conventional Fenton treatment, as denoted by the much greater drop in the achieved reduction of the CODs at higher pH values than the optimum (compare Figures 20 and 21).

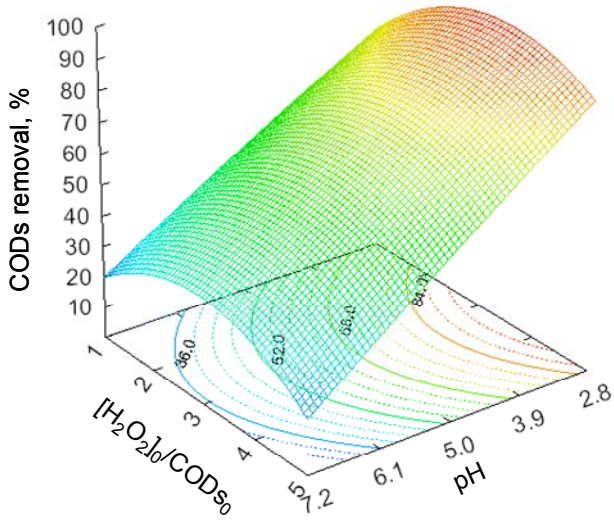

Figure 21. Response surface and contour plot for CODs removal from paper mill RO retentate by photo-Fenton treatment at T = 25 ºC and variable concentrations of reagent and pH.

However, the performed optimal photo-Fenton treatment required a lower concentration of H_2O_2 to remove more CODs than the optimal conventional Fenton treatment detailed above ($[H_2O_2]_0/CODs_0$ > 2.8; Figure 20); which denotes that Fe^{3+} to Fe^{2+} photo-reduction effectively promotes a quicker evolution of the Fenton reaction as it has been previously reported (Hermosilla et al., 2009b).

Moreover, the oxidation efficiency of the process is significantly greater for photo-Fenton (OE = 0.78) than for conventional Fenton treatment (OE = 0.64) at pH = 2.8.

The necessity of a much greater quantity of Fe^{2+} will further imply an associated higher cost for iron sludge disposal after performing the conventional Fenton treatment of RO retentate. In fact, less iron sludge generation has been reported previously when optimizing Fenton and photo-Fenton treatments of landfill leachate (Hermosilla et al., 2009a) and in the case of photo-Fenton the $[H_2O_2]_0/[Fe^{2+}]_0$ ratio may be greater than 30 (Figure 21).

4.3.1.3. TiO_2 photocatalysis treatment

Although the reduction of the CODs seemed to be almost maximized during the first hour of treatment, as reported previously in other similar trials (Dialynas and Diamadopoulos, 2008), it stepped up further from 90 min onwards (Figure 22). During the first 10 minutes of treatment (UV-lamp switched off) part of the CODs is adsorbed on TiO_2. After switching the lamp on, easily oxidizable organic matter was removed; and in a second stage, organic matter was eliminated at a much slower rate (up to ≈ 60 min). As easier-to-oxidize by-products are generated from the treatment of more recalcitrant chemicals, a higher CODs removal can be achieved. Similar successive stages may alternate prolonging the process indefinitely, so a 5 hours treatment was set as a reasonable reference to compare results. Further treatment did not seem to add significant reduction of the CODs for the investment of such an elevated reaction time and cost (Figure 22).

The overall efficiency of the process was strongly influenced by the dosage of TiO_2 (Figure 22), as it has been previously reported (Chang et al., 2004; Tanaka et al., 1999). An optimum dosage of 10 $g{\cdot}L^{-1}$ of TiO_2 was found to maximize the removal of CODs (35-40%) after a 5 hours of TiO_2 photocatalytic treatment of the sampled RO retentate, as it has been previously reported for the equivalent treatment of lignin powder (Chang et al., 2004).

Beyond these overall poorer oxidative results, it has been highlighted that the photocatalytic degradation of organic matter mainly affected those pollutants that are more reluctant to biological degradation, thus enhancing greatly the biodegradability of the wastewater (Amat et al., 2005a; Yeber et al., 2000). Therefore, TiO_2 photocatalysis may be considered as an interesting pre-oxidation step preceding biological treatment of RO retentate. In fact, biodegradability was improved along the TiO_2 photocatalytic treatment of RO retentate, even achieving figures close to those developed by ethylene glycol (≈100% CODs removal) when 10 $g{\cdot}L^{-1}$ of TiO_2 were used (Figure 23).

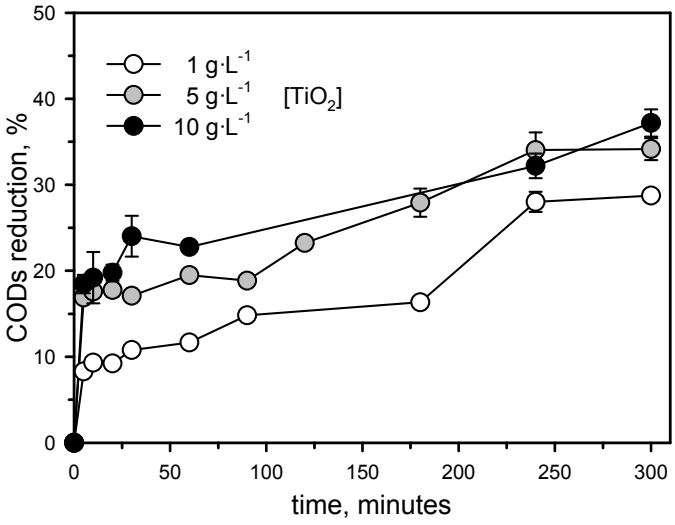

Figure 22. CODs reduction after TiO_2 photocatalysis of RO retentate at different concentrations (T = 25 ºC, initial natural pH = 7.2).

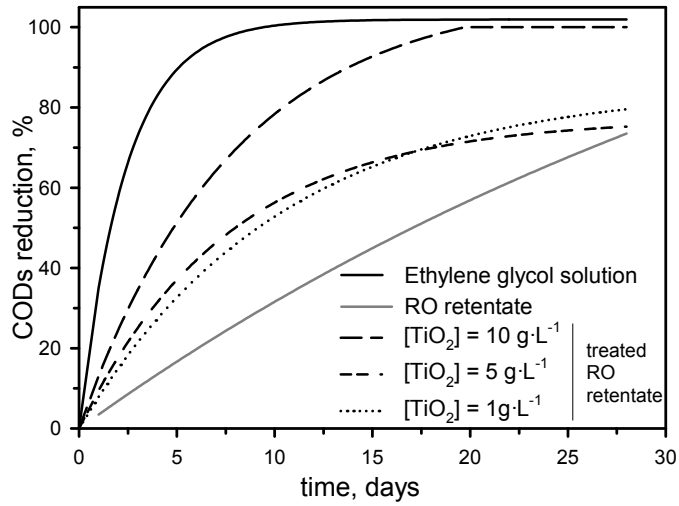

Figure 23. Biodegradability evolution along the optimal TiO_2 photocatalytic treatment of RO retentate.

5 SCAVENGERS IN PHOTOCATALYSED AOPs

One of the main problems found when trying to increase the degradation in recycled paper mill effluents by applying AOPs was the presence of oxi-recalcitrant compounds, such as bicarbonates. In addition, the influence of inorganic compounds over the efficiency of AOPs is not totally clear in the available literature. Therefore, the main objective of this section, corresponding to paper IV, is to clarify the influence of bicarbonates on photocatalysed oxidation processes and to find out the reasons for their influence. TiO_2 photocatalysis and photo-Fenton using Fe^0 as iron catalyst were performed to evaluate the influence of varied dosages of bicarbonates on these heterogeneous processes. pH changes and catalyst behaviour were also studied with and without bicarbonates trying to determine whether there is a scavenger effect or not.

In order to achieve the proposed objectives, synthetic samples of lignin were prepared in ultrapure water. The use of synthetic water allows the influence of the bicarbonates to be better understood without any other interference as real wastewaters can provide.

The concentration of lignin solution was 300 ppm and 250 mL of this solution was treated by TiO_2 photocatalysis and Fe^0 photo-Fenton. The optimum dose of TiO_2 in photocatalysis process was considered 7 $gTiO_2 \cdot L^{-1}$, based on the results obtained by Jefferson et al. (2012), although lower (5 $gTiO_2 \cdot L^{-1}$) and higher (9 $gTiO_2 \cdot L^{-1}$) dose values were checked to be sure about the optimum in the treatment of lignin.

The optimum dose of H_2O_2 for photo-Fenton process has been selected based on a theoretical stoichiometric relation between the initial CODs and the required H_2O_2 to totally oxidize the organic matter of the solution that is 2.125 (Kim et al., 1997), although higher (3.125) and lower (1.125) rates were checked for the treatment of lignin solution. Using Fe^0 instead of salts of Fe^{2+} as a catalyst avoids the use of salts during the study. The optimum molar relation between initial amounts of H_2O_2 and Fe^0 was 60, based on the degradation achieved by this catalyst, as reported by Blanco et al. (In progress).

Experiments were performed adding $NaHCO_3$ (alkalinity between 100 and 1000 $mg \cdot L^{-1}$ of $CaCO_3$) in order to check the influence of the amount of alkalinity. Alkalinity was measured as mg of $CaCO_3$ per litre and named as carbonates. A batch of trials was performed to assess the influence of the pH change on the treatment, selecting 750 ppm of $CaCO_3$ as the basis for the calculation.

A one-way ANOVA was run (SigmaPlot 11, SPSS Inc.) in order to determine the significant level of differences among experimental runs. *Post hoc* all pairwise comparisons were performed using Tukey's test ($P<0.05$).

5.1. Results

5.1.1. Alkalinity influence on TiO_2 photocatalysis treatment

A slight increase in CODs removal (≈10%) between 5 to 7 $gTiO_2 \cdot L^{-1}$ dosage was achieved, although from 7 to 9 $gTiO_2 \cdot L^{-1}$ dosage there were not significant differences, so the optimum dose was established as 7 $gTiO_2 \cdot L^{-1}$, in agreement with the previous literature (Jefferson et al., 2012).

TiO_2 photocatalysis showed a drastic decrease in efficiency from 80% CODs reduction to values between 30 and 50% at the end of the reaction, depending on the amount of $NaHCO_3$ added (Figure 24).

Initially, lignin removal was due to the adsorption of this compound on the TiO_2 surface and the dark CODs reduction was ≈70% after five contact minutes. Afterwards, the removal of lignin was due to the oxidation process.

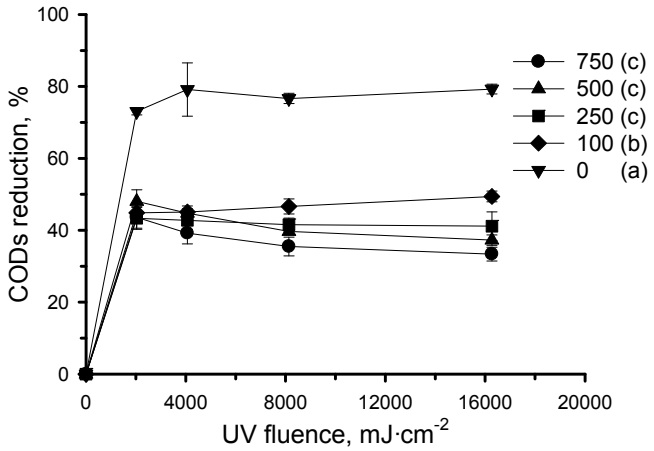

Figure 24. Carbonates concentration influence in terms of CODs reduction during TiO_2 photocatalysis treatment at different UV fluences. Letters (a,b,c) identify statistically significant differences at the end of the treatment (Tukey's test, $P < 0.05$).

Aggregation of the catalyst was observed when wastewater was prepared adding $NaHCO_3$ or NaOH (Figure 25). The aggregation implied a reduction of the available catalyst surface; hence, the efficiency associated to adsorption was also reduced.

At low carbonates concentration, 0-100 ppm of $CaCO_3$, the tendency over the course of the reaction was an initial drastic increase of the CODs removal due to the initial adsorption of the lignin on the catalyst surface, followed by no further CODs reduction and no desorption from the catalyst surface, although without the presence of carbonates the total CODs removal was almost double that with 100 ppm (Figure 24). Furthermore, over the course of the treatment without carbonates, or just adding them at a low concentration, there was a reduction of the molecules in the solution and the remaining molecules showed a lower molecular weight than those in the untreated solution (Figure 26A and 26B). Higher carbonate doses, 250-750 ppm of $CaCO_3$, showed the same initial increase of the CODs removal followed by a slight decrease in the percentage of CODs removal. The addition of a higher concentration of carbonates resulted in an increase of the molecules in the medium with a wide range of sizes (Figure 26C). Lignin together with intermediate compounds was desorbed from the TiO_2 surface during the reaction. Therefore, the amount of molecules in the solution and the CODs were slightly increased during the reaction. As a conclusion, when the presence of carbonates was lower, the efficiency

of the treatment was higher. On the other hand, a higher presence of carbonates avoided the adequate progress of this treatment.

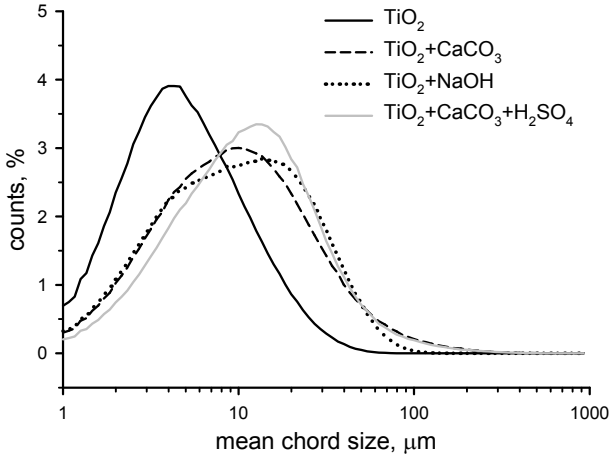

Figure 25. Chord size distribution of TiO_2 catalyst in water influenced by the addition of carbonates, NaOH and sulphuric acid and measured with FBRM.

The UV fluence applied during the treatment was raised from 16272 to 97632 $mJ{\cdot}cm^{-2}$. TiO_2 photocatalysis achieved greater CODs reduction applying the higher fluence (97632 $mJ{\cdot}cm^{-2}$) than that achieved without the addition of carbonates when the applied fluence was 16272 $mJ{\cdot}cm^{-2}$. At this higher fluence, 97632 $mJ{\cdot}cm^{-2}$, in the presence of 750 ppm of $CaCO_3$, 78% CODs reduction was obtained and by adding 100 ppm of $CaCO_3$ the process reached 95% CODs reduction. The increment of carbonates concentration caused a generation of more intermediate products with higher molecular weight which would require a greater degree of oxidation resulting in lower CODs reductions (Figure 26).

The addition of carbonates caused a pH modification in the solution. These changes could affect the process' efficiency. TiO_2 photocatalysis did not show statistical differences between increasing the pH with carbonates or NaOH, although experiments with NaOH reported lower CODs reductions. Analyses with HPSEC showed similar structure of the intermediate products obtained when treated in the presence of carbonates or NaOH (Figure 26C and 26D, respectively).

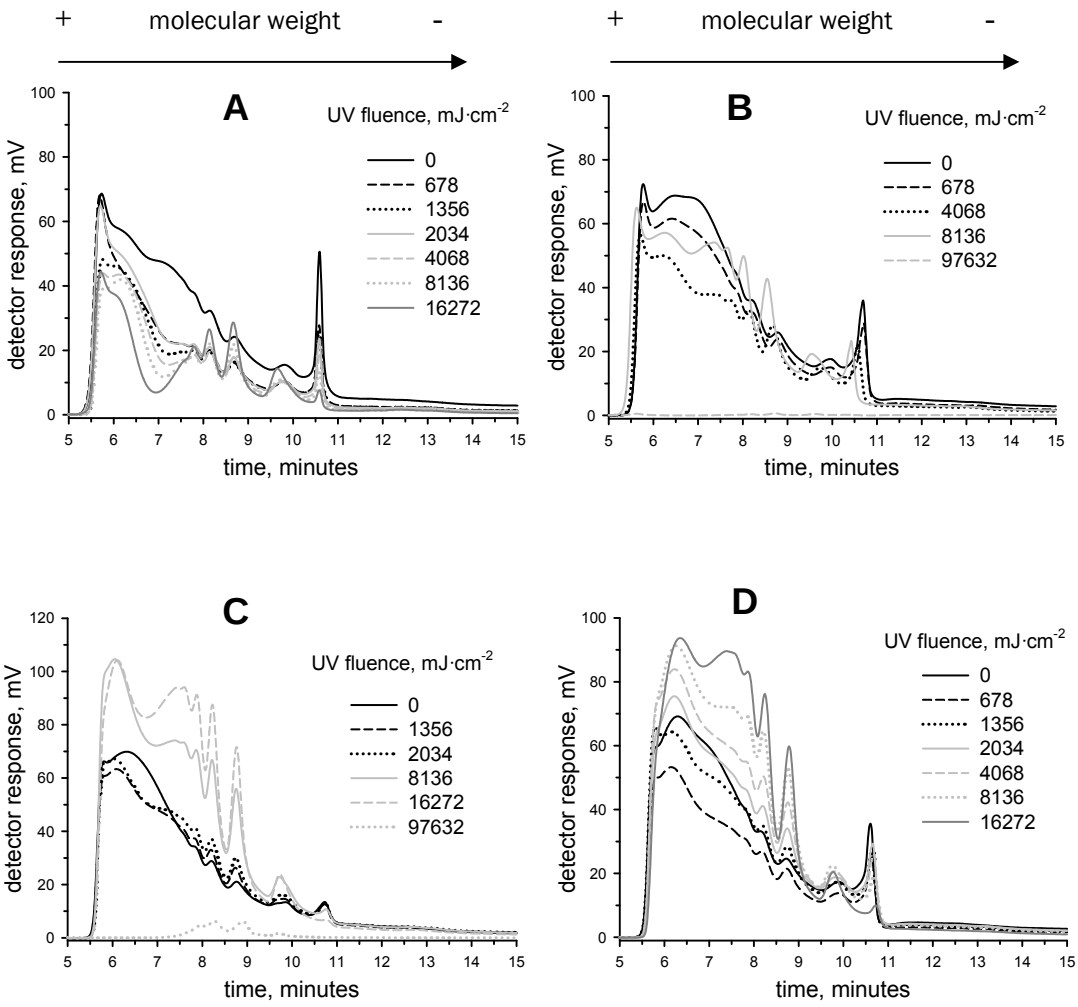

Figure 26. HPSEC analyses of the treated solution applying TiO_2 photocatalysis at different UV fluences when: A) 0 ppm of $CaCO_3$, B) 100 ppm of $CaCO_3$, C) 750 ppm of $CaCO_3$ and D) NaOH were added to the 300 mg·L^{-1} lignin solution.

The addition of NaOH to the water increased the presence of OH^- ions that competed with lignin for the sites onto the catalyst surface. As a consequence, a smaller quantity of lignin was adsorbed and oxidized and lower efficiency was achieved in the presence of NaOH. The semiconductor behaviour of TiO_2 assisted the transference of electrons through its structure. Electrons were released from the adsorbed OH^- due to a redox reaction (Fernandez, 2003). These electrons were

given up to the TiO_2 that is an acceptor, and they were moved, thus reducing the catalyst surface charge and the repulsion forces, hence favouring the particles aggregation.

A greater degree of aggregation was obtained in the experiment using NaOH (Figure 25) because the ionic strength was higher than for alkaline waters. In addition, spontaneous aggregation is favoured more in the presence of NaOH than in the presence of bicarbonates (Williams, 1992). The OH^- ions from NaOH were adsorbed on the catalyst surface, acting as a scavenger and showing a strong electron donor effect. Meanwhile, the scavenger effect of the HCO_3^-/CO_3^{2-} was not very important and the electron donor effect was lessened. That was proved due to the pH behaviour during the experiments. The addition of TiO_2 to the alkaline water did not result in a notable decrease of the pH, while in water with NaOH, the addition of TiO_2 decreased the pH drastically due to the adsorption of OH^- on the TiO_2 surface and the electron change in the interface.

In short, the experiments performed in presence of NaOH achieved worse results than the experiments performed when the solution was prepared with alkaline water. The presence of these compounds ($NaHCO_3$ or NaOH) decreased the efficiency of the process due to the aggregation of the catalyst in their presence; thus reducing the available surface for the reaction when compared with the experiments without any addition of salts.

Furthermore, sulphuric acid was added in order to decrease the pH up to the initial value of the lignin solution. When sulphuric acid was added to the solution with carbonates in order to decrease the pH to initial neutral values, the CODs reduction increased a little. This can be explained by the fact that at neutral pH values, competition for the reactive sites on the surface of TiO_2 is lower and thus the efficiency higher (Merayo et al., 2013a). However the greatest CODs reduction reached without any salts addition was not achieved. pH modification had an overall positive effect but the catalyst aggregation was not reversible and it was not possible to achieve the same efficiency. In conclusion, NaOH and carbonates decreased the efficiency of the photocatalysis process mainly due to catalyst aggregation and in part due to pH modifications.

These results applied to industrial wastewaters, such as the ones from section 4 “AOPs applied to pulp and paper mill wastewaters”, imply an important effect of the alkalinity when TiO_2 photocatalysis is used for the treatment. As long as carbonates concentration increases, TiO_2 photocatalysis efficiency decreases. That explains the low degradation achieved by photocatalysis applied to all of the industrial wastewaters. Although kraft pulp mill effluent has the lower concentration of carbonates, its degradation rate was low due to the addition of NaOH to adjust the initial pH = 5. The presence of carbonates joint to the addition of NaOH favoured the aggregation of TiO_2 (Figure 25) and the reduction of the efficiency. That also explains why at pH = 7 higher CODs reduction was reported than at pH = 12 (Figure 14). In

the same way, recycled paper mill effluents presented higher CODs reduction at pH = 7 than at pH = 12 (Figure 16). However, recycled paper mill effluent had an initial pH = 7.8 and the addition of NaOH was only added in the experiment at pH 12 and that is the reason of the close results obtained for both kraft pulp and recycled paper mill effluents at pH = 7. Finally, The RO retentates were treated without any addition of NaOH because the pH was not adjusted. Therefore, even though RO retentates had the higher amount of carbonates, TiO_2 photocatalysis achieved the higher CODs reductions compared with kraft pulp and recycled paper mill effluents. It is clear in the case of use TiO_2 that the addition of ions, especially OH^-, to the wastewater will result in lower efficiencies.

5.1.2. Alkalinity influence on photo-Fenton treatment using Fe^0

When the $[H_2O_2]_0/CODs_0$ relationship was 1.125 the lowest CODs removal (about 14% lower) was obtained, and the differences between the 2.125 and 3.125 relations were not statistically significant. Therefore, the selected $[H_2O_2]_0/CODs_0$ relation was 2.125.

The experiment with photo-Fenton reported around 40% CODs removal without carbonates addition under the best treatment conditions (Figure 27). The differences between TiO_2 photocatalysis and photo-Fenton were due to the solution pH (≈6.5) being far from optimum for the photo-Fenton process, that is, 2.8 (Hermosilla et al., 2012). Moreover, photo-Fenton treatment using Fe^0 as the catalyst generally works better at acidic pH values (Fu et al., 2010). This behaviour is due to the solubilization of the iron species at pH values lower than 4 (Son et al., 2009). In addition, Fe^0 is oxidized to Fe^{2+} in aqueous acid conditions on the catalyst surface giving the optimized pH value of 3 (Devi et al., 2009; Fu et al., 2010).

Concerning the photo-Fenton process, carbonates demonstrated a little influence over the process efficiency. CODs reduction after 2 hours was the same when the carbonates concentration was zero and when there was 250 ppm of $CaCO_3$. In addition, differences in CODs reductions with higher carbonates doses were smaller than in photocatalysis (Figure 27). As described above, CODs reduction decreased from 80% when no carbonates were added to around 40% when 750 ppm of $CaCO_3$ were added during photocatalysis treatment; however, during the photo-Fenton process, the CODs reduction decreased ~5%. Fe^0 was studied in order to find out if carbonates had any influence on catalyst behaviour and consequently, on the efficiency. The presence of carbonates produced a low degree of aggregation of the Fe^0 catalyst and it was related to the small decrease of CODs removal achieved in the presence of carbonates. This aggregation, and that observed with TiO_2 under the same conditions were due to the increase in the ionic strength that reduced the electrostatic forces thus favouring the aggregation. This increment of the ionic strength was produced by the addition of charges (HCO_3^- and Na^+).

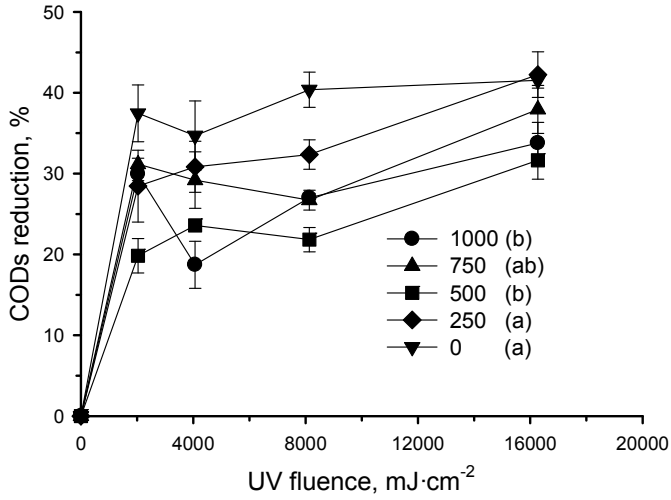

Figure 27. Influence of the amount of carbonates on the CODs reduction during the photo-Fenton treatment at different UV fluences. Letters (a,b) identify statistically significant differences at the end of the treatment (Tukey's test, $P < 0.05$).

In the photo-Fenton experiments at higher doses of carbonates (750 and 1000 ppm of $CaCO_3$), an initial increase is observed followed by a decrease in CODs reduction at the beginning of the experimental time, finishing with a continuous degradation tendency. This can be explained by the aggregation of the catalyst, which promotes the slower evolution of the whole reaction. Lower doses (250 and 500 ppm of $CaCO_3$) showed a higher oxidation at the beginning of the reaction with subsequent lower kinetics (Figure 27). A study of the structure of the molecules involved in the treatment was also conducted using HPSEC analyses (Figure 28). The HMW lignin polymer was broken down by photo-Fenton treatment during the first minutes of the reaction generating intermediate products with LMW. There were no differences in the formation of intermediate products when varying amounts of carbonates were added to the wastewater (Figure 28). The main mechanism for lignin degradation was oxidation not adsorption. As a consequence, interference by carbonates is lower and only due to the small decrease of the catalyst surface when aggregation occurred, thus allowing less available surface area and lessening the oxidation-reduction reactions on the Fe^0 catalyst surface, hence lowering the reaction kinetics.

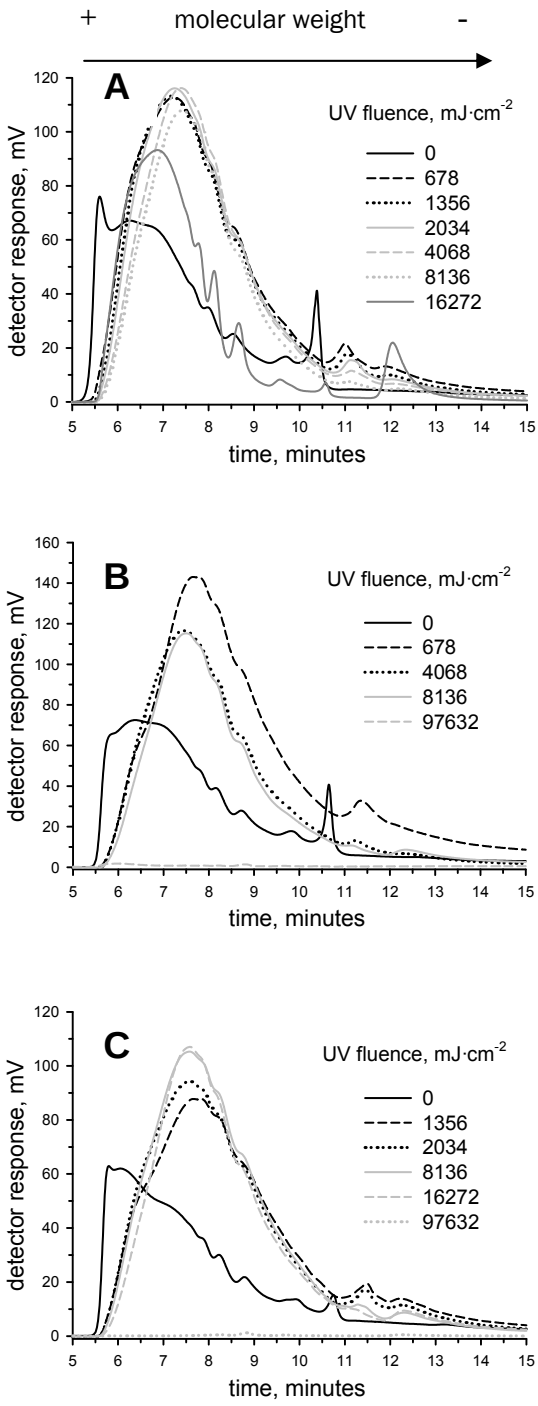

Figure 28. HPSEC analysis of the treated solution applying photo-Fenton at different UV fluences when: A) 0 ppm of $CaCO_3$, B) 250 ppm of $CaCO_3$, and C) 750 ppm of $CaCO_3$ were added to the 300 $mg{\cdot}L^{-1}$ lignin solution.

For the photo-Fenton treatment, by applying 97632 mJ·cm^{-2} of UV fluence a strong improvement in treatment efficiency for high and low carbonates concentration was achieved. When the carbonates concentration was 750 ppm of $CaCO_3$ a 92% CODs reduction was achieved and 250 ppm of $CaCO_3$ reached 93%, proving that the concentration of carbonates had very little effect on this treatment. This increment in the applied fluence allowed a drastic increase in the CODs reduction despite the presence of carbonates and the unfavourably high pH value.

The experiments studying the influence of pH on photo-Fenton treatment behaved completely different to those involving photocatalysis. A strong decrease in efficiency was noted when NaOH was used to reach the same pH values than in the experiment where carbonates were added (Figure 29). In this case, the OH^- ions were adsorbed on the Fe^0 surface. Adsorbed OH^- ions avoided the oxidation-reduction reactions on the catalyst surface resulting in a reduction of process efficiency. During this experiment the pH did not decrease after iron addition. Therefore, electron transference was not favoured and the OH^- ions kept being adsorbed onto the Fe^0 surface, both increasing repulsion forces between particles and avoiding the aggregation of the catalyst, although some degree of aggregation can be observed.

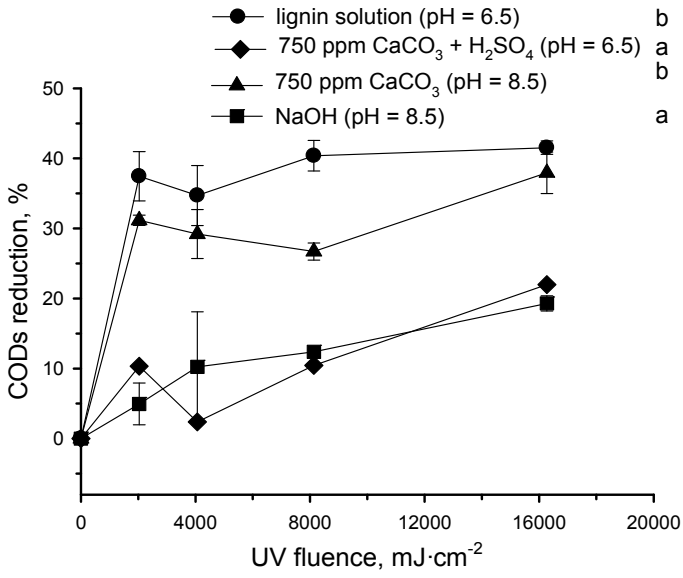

Figure 29. pH influence on the photo-Fenton treatment, studied at pH ≈ 6.5 without any salt addition and adding 750 ppm of $CaCO_3$ (pH control by H_2SO_4); and also studied at pH ≈ 8.5 (pH obtained after the addition of 750 ppm of $CaCO_3$) obtained by addition of $NaHCO_3$ or NaOH. Letters (a,b) identify statistically significant differences at the end of the treatment (Tukey's test, $P < 0.05$).

Sulphuric acid was added to the experiment with 750 ppm of $CaCO_3$ in order to recover the pH of the solution when there was no salt added, with the aim being to improve the efficiency of the process. However, it resulted in a greater decrease in the efficiency than the experiment with 750 ppm of $CaCO_3$. Once the carbonates were added to the solution, pH modifications did not imply better results, as the addition of ions to the solution had an important influence on the catalyst behaviour (Figure 29). It is likely that the newly added H^+ ions reacted with active sites on Fe^0 surface, further reducing the available surface for the Fenton reaction and, hence reducing the efficiency of the process, as was the case with the addition of NaOH. Fe^0 showed an electron donor effect by releasing the electrons that are recombined with H^+ present in the wastewater.

6 NEW MONITORING TOOLS FOR AOPs

A precise and real time control of the AOPs to improve their performance is nowadays a must. The application of the knowledge provided by the on-line control of the compounds involved at each moment of the reaction is important in order to optimize the reagents and operational conditions. In addition, the real time information would allow to better understand the mechanisms of the reactions, to recognize the modifications over the mechanism due to interfering compounds and to predict the final treatment efficiency. In addition, the process bottlenecks and their solutions can be identified in a faster and easier way.

The reaction control can be performed in several ways. Commonly, periodical samples are taken for their analysis in the case of the AOPs. One or more water quality parameters are measured in order to assess the reaction progress and to

optimize the process. There are also more sophisticated techniques for the process control, among them liquid and gas chromatography, infrared spectroscopy, ultraviolet-visible spectrophotometry, etc. However, neither of them has ever been applied on-line for monitoring the oxidation processes in real time. As a consequence, this section is focused on the development of a new methodology that allows real time monitoring of the AOPs reactions. The new methodology was validated by its application in a Fenton process using a model compound (phenol), a real NP recycled paper mill effluent and a scarcely studied industrial priority pollutant (1,4-dioxane). These studies are published in papers V and VI.

6.1. Development of on-line FTIR methodology to monitor the Fenton process

To facilitate the interpretation of the data, methodology was developed working with synthetic waters. The concentration of phenol (16 mmol in a total volume of 100 mL) was fixed in order to achieve a good monitoring resolution of the process in the ReactIR iC10 device.

The concentrations of reagents were chosen to meet the following ratios: $[H_2O_2]_0/COD_{S0} = 2.15$, and $[H_2O_2]_0/[Fe^{2+}]_0 = 37.5$; as these reaction conditions have previously been reported to produce optimal Fenton treatment results for the target substances at pH = 2.8 (Hermosilla et al., 2009b; Kavitha and Palanivelu, 2004). 100 mL of the prepared solution was treated under these conditions. H_2O_2 was added in continuous mode allowing the use of the added quantity of H_2O_2 (milimol), rather than the reaction time, as an indicator of the progress and evolution of the oxidation treatment.

6.1.1. Results and discussion

Results obtained from the Fenton degradation of a synthetic solution of phenol show that three repetitions of every performed experiment reproduced the same results, and there were no meaningful differences among them.

Spectra within the region of 650 to 2000 cm^{-1} continuously increased during H_2O_2 addition until 60 mmol of H_2O_2 were added in total and the greatest absorbance was reached. Subsequently, the spectra began to decrease and their peaks progressively became smoother (Figure 30).

After the first addition of H_2O_2, the colour of the solution instantaneously changed from colourless to dark brown (almost black) due to the oxidation of Fe^{2+} to Fe^{3+} and the generation of quinones (i.e. hydroquinone and benzoquinone, Figure 31) in redox equilibrium (Yalfani et al., 2009; Zazo et al., 2005), which are more

toxic than phenol itself (Zazo et al., 2005). This dark colour gradually lost its intensity thereafter and a pale orange colour remained after adding a total 160 mmol of H_2O_2 (when its ratio to the initial amount of phenol was 10) because quinones have already been degraded; as well as due to the remaining presence of several by-products of acid formation stages (oxalic acid, mainly) (Hermosilla et al., 2009b; Yalfani et al., 2009) that are able to reduce Fe^{3+} back to Fe^{2+} (Manahan, 2010). Similar colour changes have been addressed before (Kavitha and Palanivelu, 2003; Yalfani et al., 2009). Furthermore, HPLC analyses confirmed these FTIR results.

The evolution of mean oxidation number of organic carbon (MOC) over the course of the treatment (Figure 31) also supports this affirmation, linearly changing from an initial value of -0.67, which is characteristic of phenol, to ≈3, which has previously been addressed to a mix of carboxylic acids where oxalic (MOC = 3) dominates (Hermosilla et al., 2009b); and it then remained constant thereafter.

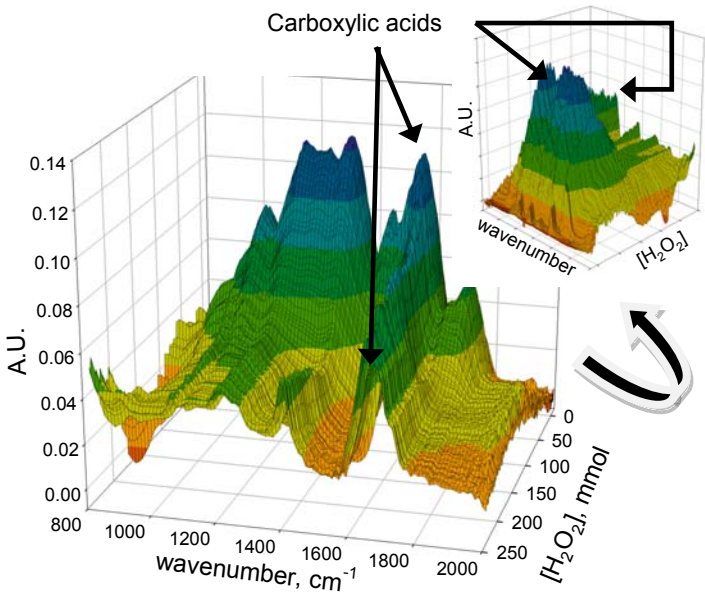

Figure 30. Evolution of FTIR-spectra along a continuous H_2O_2 addition in the Fenton oxidation of phenol. The presence of the evolution of carboxylic acids is highlighted, and a turned around graph is also shown in greater detail. (Reaction conditions: room temperature (≈20-25ºC); pH = 2.8 ± 0.2; 16 mmol phenol; $[H_2O_2]_0/CODs_0 = 2.15$; $[H_2O_2]_0/[Fe^{2+}]_0 = 37.5$).

The concentration profile of phenolic compounds turned out to be mainly integrated by phenol itself and some products that are generated by its hydroxylation, namely hydroquinone, benzoquinone (Kusic et al., 2006; Yalfani et al., 2009; Zazo et al., 2005) and catechol (Figure 31). On the other hand, resorcinol was not actually found along the Fenton oxidation of phenol. In fact, its formation would rather be implausible based upon the substitution rules of organic chemistry (Yalfani et al., 2009).

The absorbance concentration profile of phenolic compounds logically increased as phenol was added to the solution; and it also grew again after the addition of H_2O_2 because other phenolic intermediate compounds of the reaction were newly formed (Figure 31). During the reaction, this phenolic mix totally disappeared when the concentration ratio between the added H_2O_2 and the initially supplied amount of phenol was close to 8, coinciding with previously reported results on the Fenton oxidation of phenol and nitrophenol, when a MOC value characteristic of the predominant presence of carboxylic acids (≈2.5-3) was kept more or less constant as the reaction progressed (Figure 31) (Hermosilla et al., 2009b).

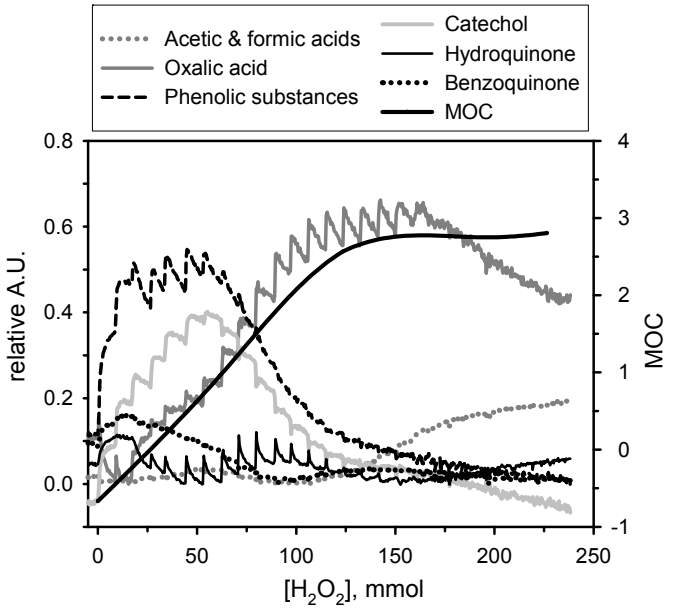

Figure 31. Absorbance profiles for main by-products, and evolution of the MOC along a continuous H_2O_2 addition in the Fenton oxidation of phenol (Reaction conditions: room temperature (≈20-25ºC); pH = 2.8 ± 0.2; 16 mmol phenol; $[H_2O_2]_0/CODs_0$ = 2.15; $[H_2O_2]_0/[Fe^{2+}]_0$ = 37.5).

Achieving the total degradation of hydroquinone is of environmental concern due to its high toxicity, which is several orders of magnitude higher than that attributed to phenol itself (Oller et al., 2007). On the other hand, catechol also turned out to be totally removed at the end of the reaction, as it has been clearly addressed by HPLC measurements. Nevertheless, catechol is highly biodegradable (Pramparo et al., 2012; Zeyaullah et al., 2009); thus, it might be further treated by biological technologies, which are, in general, cheaper treatments than AOPs.

Furthermore, previous results reporting a greater production of catechol than hydroquinone along the process seemed to be confirmed (Pontes et al., 2010; Yalfani et al., 2009), as it shows when comparing the concentration profiles of both compounds in Figure 31. In short, catechol and hydroquinone were initially formed as phenol disappeared; and then, they began to be gradually degraded, competing with their own further formation as phenol was still being oxidized.

In addition, phenol decreased its concentration in the solution faster than the other newly generated phenolic intermediates (hydroquinone, benzoquinone, and catechol) of the reaction (comparing Figures 31 and 32); which is also in accordance to previous scientific reports (Hermosilla et al., 2009b; Pontes et al., 2010; Yalfani et al., 2009). Only 4% of phenol remained after adding a ratio of H_2O_2 to phenol of 3.9; results that were further confirmed by HPLC analyses.

At this point, the removal of CODs was higher than 50%, and it did not show further lineal progress (Figure 32). Finally, phenol turned out to be totally degraded when the aggregated concentration of H_2O_2 reached 5.6 times the initial amount of added phenol, and the reduction of the CODs was close to 75%; showing a further asymptotic evolution because of the growing presence of carboxylic acids, which are more difficult to oxidize. Hereafter, the mix of phenolic compounds remaining in the solution was mainly made up by hydroquinone and catechol (Figure 31), the absorbance concentration profile of which quickly decreased until the ratio between the total added H_2O_2 and the initial amount of phenol was close to 6.5. Then, its abatement thereafter progressed smoothly, and its total degradation was finally achieved when this ratio reached approximately 8, as confirmed by HPLC determinations.

Some carboxylic acids remained in the solution at the end of the process as the main persistent by-products of the oxidation treatment of phenol (Figure 30); although they are also considered highly biodegradable and might be further treated by biological processes (Mantzavinos and Psillakis, 2004; Oller et al., 2007). Oxalic, acetic, and formic acids were identified as the resultant products of an acid formation stage within the process. Its presence and persistence was also confirmed by HPLC measurement, and MOC and CODs behaviour assessment (Figures 31 and 32), as previously stated. That is, its presence stayed constant after the ratio of total added H_2O_2 to the initial amount of phenol reached a value close to 8, which was

accurately measured by HPLC; and was also confirmed by a non further change of MOC from characteristic values previously addressed for carboxylic acids mix (Hermosilla et al., 2009b), although CODs was still being removed in small quantities (Figures 31 and 32).

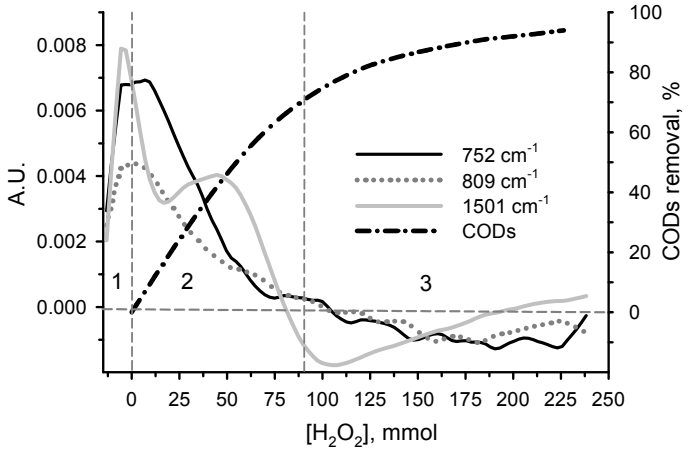

Figure 32. Smooth absorbance concentration profiles of phenol and evolution of the removal of the CODs along the Fenton oxidation of phenol considering all its three typical detection wavenumbers (752, 809, and 1501 cm^{-1}). Note: 1= addition of reagents; 2= progressive removal of phenol; 3= after the total removal of phenol.

In short, carboxylic acids were probably formed by ring-opening reactions that take place during the degradation stages of some aromatic intermediate products of the reaction (Hermosilla et al., 2009b; Pontes et al., 2010; Yalfani et al., 2009). Whilst the presence of oxalic acid was detected almost from the beginning of the reaction (Figure 31), when the ratio of total added H_2O_2 to the initial concentration of phenol was just 1.8; acetic and formic acids presence was noticed in the solution when this ratio reached 6.25, suggesting that these two carboxylic acids may be generated by the degradation of some other intermediate reaction by-products.

All these carboxylic acids that are inevitably formed during the oxidative degradation of phenol are more or less recalcitrant to its further Fenton oxidation treatment (Abbas et al., 2008; Bigda, 1995); so they will hereafter be considered as

oxi-recalcitrant compounds (Hermosilla et al., 2009b). In fact, this limited capacity to degrade carboxylic acids is one of the main drawbacks for achieving the total mineralization of phenol by Fenton's reagent (Hermosilla et al., 2009b; Yalfani et al., 2009). Therefore, the main objective of AOPs based treatment steps might be defined as controlling the process until a maximum biodegradability threshold is achieved in order to combine this treatment with a cheaper posterior biological stage (Hermosilla et al., 2012).

In summary, a final 94% reduction of the CODs was achieved (Figure 32), which is even higher than previously reported results (Hermosilla et al., 2009b; Kavitha and Palanivelu, 2004). The continuous addition of H_2O_2, which has previously been proved to enhance the removal of CODs in comparison to batch mode (Hermosilla et al., 2009a), as well as the steady thorough control of the reaction conditions that was performed, have surely contributed to achieving this very successful result. The remaining 6% of CODs was held by the remaining mix of oxi-recalcitrant by-products, oxalic and mainly other carboxylic acids.

6.2. Application of on-line FTIR for the degradation of a real pulp and paper industrial wastewater and 1,4-dioxane

The on-line FTIR methodology was used to monitor the degradation of the real NP recycled paper mill effluent used in section 4.2. Although this wastewater was the most concentrated among those studied in section 4 "AOPs applied to pulp and paper mill wastewaters", the sensitivity of the FTIR probe did not allow to obtain any signal, apart from water and carbonates. Therefore, it is not possible to use this particular probe for the real industrial wastewaters and more sensitivity probes are needed for this kind of applications. The evolution since the first steps of FTIR analysis of liquid samples from the beginning of the 1980s until 2005, when React IR iC10 was developed by Mettler-Toledo, has been very important. The history of ReactIR has been evolving towards more sophisticated probes that provide increased sensitivity (development of Bell Style AgX Fiber probe in 2006). The maximum sensitivity has been achieved through the elimination of transfer optics which allows the use for low concentration chemistries (ReactIR DS Micro Flow Cell developed in 2010), which could be the appropriate probe for the on-line control of AOPs treatment in industrial wastewaters.

However, the study of the degradation of some specific pollutants present in wastewaters can help significantly to find out the optimum process conditions for the combinations of AOPs and biological processes. These tailor-made processes will focus on the degradation of the target compounds into biodegradable products in order to remove them from final effluent and to accomplish the Water Framework Directive (Directive 2000/60/EC). Thus, a synthetic solution of 1,4-dioxane was

used because it is a non-biodegradable, toxic, hazardous, and priority pollutant widely used in the chemical industry as a solvent; as well as it is a resulting by-product of many industrial processes. It can be also used in pulp and paper industry as additive in ozone bleaching of a kraft pulp (Ni and Ooi, 1996) or in the soda-dioxane pulping of cotton linter to stabilized the long chain cellulose macromolecules (Abd El-Ghany, 2012). Furthermore, it cannot be treated by conventional bio-treatment technologies, as well as physical and some chemical treatments have not reported good results for its removal.

RSM was used as a statistical method to evaluate the influence and interaction between variables for the optimization process. RSM was performed using H_2O_2 concentration levels as dependent ratios $[H_2O_2]_0/CODs_0$: 1.062, 2.125 and 4.250; $[H_2O_2]_0/[Fe^{2+}]_0$ molar ratios of 1.0, 5.0 and 10.0; and, pH levels of 2.8, 5 and 7.2 for the Fenton treatment. RSM regression analysis was performed according to a full factorial design (N = 27).

500 mL of 1,4-dioxane solution (2.81 mmol·L^{-1} of 1,4-dioxane; initial CODs of 450 mg·L^{-1}) for the optimization process and 100 mL (70 mmol·L^{-1} of 1,4-dioxane) for the degradation monitoring with FTIR were used for the Fenton degradation of the 1,4-dioxane. Ferrous sulphate and H_2O_2 were added to achieve the desired reagents concentrations. H_2O_2 was added in batch mode for the optimization experiments and in continuous mode for FTIR experiments (8.8 mmol H_2O_2·min^{-1}).

6.2.1. Results and discussion

6.2.1.1. Optimization of conventional Fenton treating 1,4-dioxane

Acidic pH avoids iron precipitation as $Fe(OH)_3$ because the solubility of iron increases (Kiwi et al., 1993) and, as a consequence, the efficiency of the process also increases. These pH values also avoid H_2O_2 decomposition (Pulgarin and Kiwi, 1996) and the scavenger function of inorganic carbons because under pH = 4.5, carbonates are removed from the solution like CO_2.

Working at lower pH values, greater CODs removal was noted (Figure 33). The difference regarding CODs reductions between working at low or high pH values was more noticeable at higher doses of H_2O_2, which is to say, a higher $[H_2O_2]_0/CODs_0$ ratio, while at lower doses of H_2O_2, the pH influence was very slight (less than 10%). The optimum pH value was 2.8, as it was also found in the treatment of the RO retentate (section 4.3.1.1). The highest influence of the pH happened at ratio of $[H_2O_2]_0/CODs_0$ = 4.25 and an acceptable CODs removal was obtained when the process was performed at pH = 7.2, more than 50%, compared with the optimized pH value of 2.8, that obtained 65% of CODs removal (Figure 33). This shows the

possibility to treat the wastewater without the use of chemicals for controlling the pH.

Higher levels of CODs removal were achieved when more concentration of H_2O_2 was used compared to the initial CODs value (Figures 33) because, in general, when there is more H_2O_2 available there is more formation of OH·, although in excess it could scavenge OH·, thus reducing the efficiency (Hermosilla et al., 2009a). In fact, this rate between initial H_2O_2 concentration and initial CODs had the highest influence on the CODs reduction. By increasing the amount of H_2O_2 added to the solution, the use of a higher pH can be counterbalanced, thus achieving a global increase in the CODs reduction (Figure 33). The molar rate between reagents, $[H_2O_2]_0/[Fe^{2+}]_0$, was the second parameter to have an influence on the process efficiency. Its negative coefficient shows that the CODs removal increased when this rate decreased, so at a fixed value of H_2O_2, higher amounts of Fe^{2+} achieved greater CODs reduction. The last factor that influenced the process was the pH (Figure 33), but, as mentioned before, its influence depends on the amount of H_2O_2 added to the process.

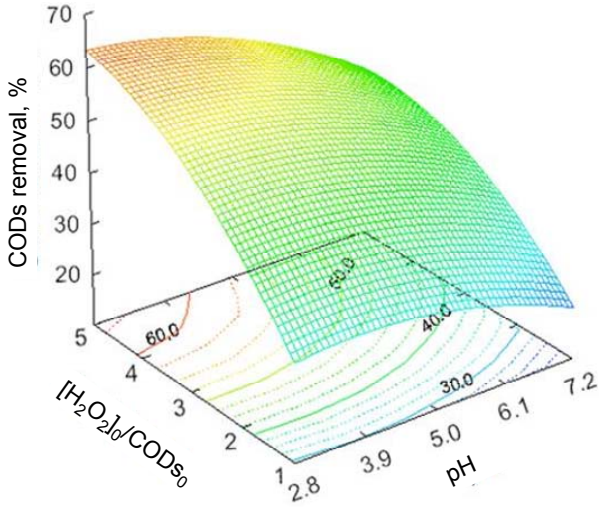

Figure 33. Response surface and contour plot for CODs removal of 1,4-dioxane solution (2.81 mmol·L^{-1}) by Fenton method at variable pH and reagents concentrations (T = 25 ºC).

The best conditions tested obtained 65% CODs removal (pH = 2.8, $[H_2O_2]_0/CODs_0$ = 4.25 and $[H_2O_2]_0/[Fe^{2+}]_0$ = 1). The remaining CODs was characterized by a 120% increase of volatile fatty acids from 33 to 72.5 $mg{\cdot}L^{-1}$, that involves a high increase in biodegradability of the final solution. Therefore, 1,4-dioxane was degraded to obtain more biodegradable organic acids, in agreement with Ghosh et al. (2010) who reported an almost total destruction of 1,4-dioxane with a decrease in the pH due to the formation of organic acids. Degradation of 1,4-dioxane resulted in biodegradable products rather than CO_2 due to the increase in biodegradability in agreement with Khan et al. (2009). Optimum conditions chosen for further experimentation were: pH = 2.8, $[H_2O_2]_0/CODs_0$ = 2.125 and $[H_2O_2]_0/[Fe^{2+}]_0$ = 5, instead of the best conditions due to the fact that a greater reagents dosage involves a proportional increase in associated cost, that are not justified for its real application. Under these conditions, 43% CODs removal was achieved and the increase in volatile fatty acids was 51%, from 38.5 to 58 $mg{\cdot}L^{-1}$, that implies an increase in biodegradability of the final solution.

6.2.1.2. Degradation monitoring of 1,4-dioxane

The Fenton reaction applied to the degradation of 1,4-dioxane was monitored with the on-line FTIR probe to obtain the concentration profiles of the main compounds presented in the reaction medium (Figure 34). FTIR spectra did not show any effect after the addition of H_2SO_4 on the studied region of spectra at this low concentration (Figure 35). It shows that the degradation towards ethylene glycol, due to the reduction of pH, is too slow to detect its formation at the beginning of the reaction. It was also verified by chromatography that no ethylene glycol had been formed before the addition of Fenton's reagent.

Before any addition of H_2O_2, there was 1,4-dioxane and $FeSO_4{\cdot}7H_2O$ in the solution. After the H_2O_2 additions a red-brown colour appeared, which implied iron oxidation from the Fe^{2+}, pale green in colour, to the Fe^{3+}, a red-orange colour; remaining a final intense orange in the solution during the reaction. When 8.8 mmol of H_2O_2 ($30\%_{w/w}$) were added to the reaction medium, ethylene glycol began to increase as well as glycolic acid and oxalate anion; whereas the profile of 1,4-dioxane began to decrease (Figure 34). After 35 mmol of H_2O_2 were fully added, glycolic acid and oxalate anion reached a maximum of absorbance and began to decrease their profile thereafter. On the other hand, the presence of formic acid was newly detected at this point, and increased exponentially reaching a constant value at the end of the reaction. After the addition of all the 70.5 mmol of H_2O_2, the reaction evolved until there was complete reduction of the 1,4-dioxane. Moreover, the profile of ethylene glycol slightly decreased as the glycolic acid and oxalate anion increased their profile at a similar linear pace, denoting certain relationship between both trends towards the end of the process. The dependence of oxalic acid on the

pH caused the appearance of the corresponding oxalate anion (Merayo et al., 2013b).

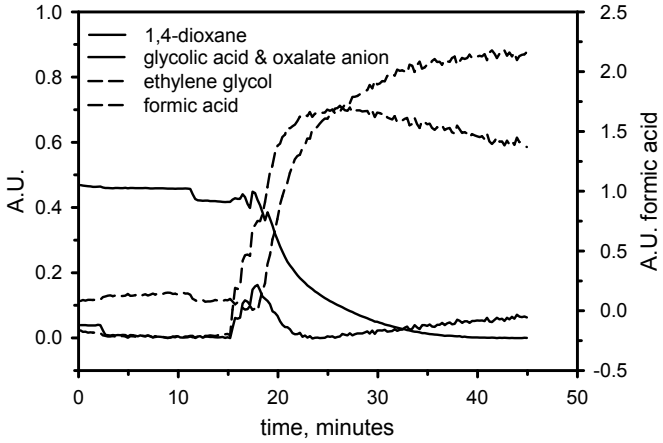

Figure 34. Absorbance profiles for main by-products along the Fenton oxidation of 1,4-dioxane. Conditions: 1,4-dioxane = 70 mmol, pH = 2.8±0.2, $[H_2O_2]_0/CODs_0$ = 2.125, $[H_2O_2]_0/[Fe^{2+}]_0$ = 5.

Chromatographic analyses confirmed the presence of all these compounds at the same moments of the reaction and the full removal of 1,4-dioxane at the end of the Fenton treatment. Therefore, the same process evolution shown in Figure 34 was confirmed by the performed chromatographic determinations at singular reaction moments. Particularly, IC analyses indicated that glycolic acid was produced in a small quantity, while the amount of oxalate was very high. This might have been the result of a fast degradation of glycolic acid into oxalic acid, which may actually be the main responsible of the detected trend.

A mechanism for the 1,4-dioxane degradation by the Fenton process has been proposed based on a radical reaction mechanism (Schemes 1-3, Paper VI). The OH· generated during the reaction between Fe^{+2} and H_2O_2, attacked the 1,4-dioxane molecule to form 1,4-dioxanyl radical. Thereafter, this reaction proceeded until 1,4-dioxan-α-oxyl radical was obtained by the reaction of 1,4-dioxanyl radical with available dissolved oxygen, first resulting in the formation of the peroxyl radical that next underwent termination reactions to generate the tetroxide precursor of 1,4-dioxan-α-oxyl radical, which was finally produced releasing oxygen (Beckett and Hua, 2003; Kim et al., 2008; Stefan and Bolton, 1998). Thereafter, 1,4-dioxan-α-oxyl

radical progressed splitting the C-C bond which was stabilized by ring opening. The linear peroxyl radical evolved then reacting with oxygen to obtain a linear tetroxide that could undergo two reactions: (1) the electrocyclic process of this linear tetroxide to obtain ethylene glycol diformate (Beckett and Hua, 2003; Stefan and Bolton, 1998); or (2) the decomposition of two alkoxyl radicals followed by β-fragmentation and H abstraction to obtain ethylene glycol monoformate (Stefan and Bolton, 1998). Stefan and Bolton (1998) also proposed another degradation pathway from the 1,4-dioxan-α-oxyl radical through the formation of methoxyacetic acid resulting in the formation of acetic acid. Although some peaks that appeared along the reaction could be identified as methoxyacetic acid and chromatographic analyses showed this by-product was produced in a small extent, the almost complete absence of acetic acid along the reaction actually denotes that this degradation alternative was not significantly followed in comparison to the degradation pathway through ethylene glycol. Nevertheless, Beckett and Hua (2003) reported that degradation of methoxyacetic acid may result in the generation of glycolic acid and formic acid.

The ethylene glycol mono- and diformate underwent an acid hydrolysis obtaining ethylene glycol and formic acid as by-products (Vollhardt and Schore, 2000). Finally, ethylene glycol can be degraded to glycolic acid that evolved to oxalic acid by deformilation (Maurino et al., 1997). The oxalic acid form at the solution pH is as oxalate anion.

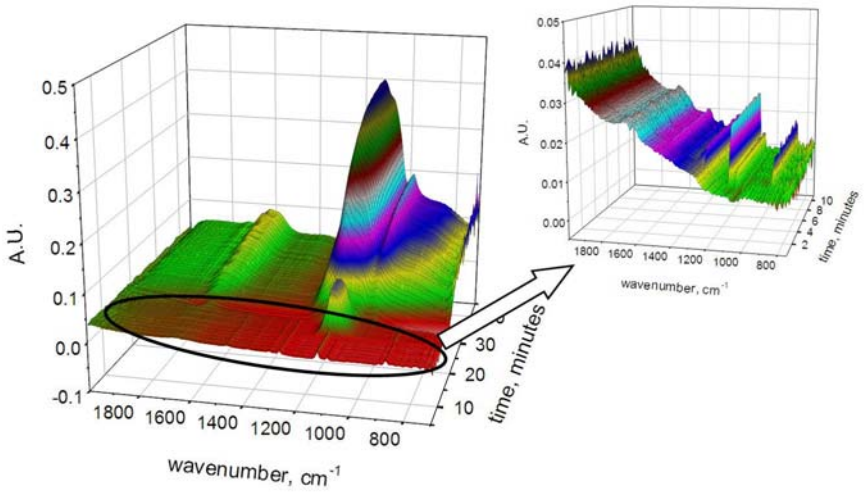

Figure 35. Evolution of the FTIR spectra of 1,4-dioxane under Fenton treatment in the 2000-750 cm^{-1} spectral region. Conditions: [1,4-dioxane] = 70 mmol, pH = 2.8 ± 0.2, $[H_2O_2]_0/CODs_0 = 2.125$, $[H_2O_2]_0/[Fe^{2+}]_0 = 5$.

7 CONCLUSIONS

The work carried out in this doctoral thesis has generated new knowledge on the applicability of AOPs to the removal of contaminants in pulp and paper industry wastewater. Different considered AOPs showed a different behaviour depending on the treated wastewater and operational conditions. The influence of scavenger substances (alkalinity) on AOPs has been assessed, and a new methodology has been developed to control and optimize Fenton reactions.

The viability of AOPs for the treatment of different pulp and paper mill effluents of different composition were assessed. In addition, combinations of AOPs with biological treatments were considered in order to improve the water quality of the most biodegradable effluents, thus reducing the overall treatment cost.

- Kraft pulp mill effluent always reported better results than recycled paper mill effluent when they were treated by AOPs. Ozonation achieved a 57% CODs reduction for the kraft mill effluent, and a 35% for the effluent from

the recycled paper mill. Whereas photocatalysis achieved lower CODs reductions in the treatment of both effluents, namely: a 28% reduction for the effluent from a kraft pulp mill, and a 24% for the effluent from the recycled paper mill, under the best designed reaction conditions.

- As a consequence of the highly biodegradable nature of the recycled paper mill effluent, it was successfully treated by MBR. A high level of organic matter reduction was obtained, resulting in the removal of an 80% of its CODs. Different combinations of AOPs with biological treatment were checked for this effluent in order to improve degradation rates. Only the combination of MBR with an ozonation post-treatment reported some improvements over MBR treatment alone; 90% of COD and 93% of colour reductions were obtained by this treatment combination. An increase in the biodegradability of the wastewater was also achieved, therefore allowing the potential successful recirculation of the resultant effluent to the MBR again.

- The RO retentate from a recycled paper mill also led to lower levels of CODs reduction when the photocatalytic treatment was applied in comparison with Fenton and photo-Fenton treatments. The photo-Fenton process was the most effective, achieving 100% of CODs and TOC removals. Furthermore, it resulted cheaper than conventional Fenton process at higher CODs reduction treatment thresholds. However, Fenton process was able to achieve an acceptable high CODs reduction (>60%) without adjusting the initial pH value of the solution, which is close to neutral.

- TiO_2 photocatalysis increased the biodegradability of a highly concentrated RO retentate enough to consider its combination with a posterior biological step in order to achieve an almost total reduction of the CODs.

The influence of alkalinity on photocatalysed processes was assessed, as well as its effect on the behaviour of the catalyst. It was found that this influence depends on specific treatment conditions. Finally, the effect of carbonate on process efficiency was mainly ascribed to their influence on the catalyst's behaviour.

- Photocatalysis treatment using TiO_2 as the catalyst showed a reduction in efficiency when treating a lignin solution in presence of bicarbonates. The TiO_2 photocatalysis degradation mechanism is mainly based on the adsorption of compounds on the catalyst surface and their posterior oxidation. The principal reasons for this decreased efficiency were TiO_2 particles aggregation and pH modification in the solution when carbonate was added.

- Photo-Fenton treatment using Fe^0 as a heterogeneous catalyst showed a slight influence of carbonate on process efficiency. Photo-Fenton with Fe^0

mainly based its mechanism of action on the oxidative process occurring on the surface of the catalyst, and the presence of carbonate did not affect this process strongly.

A new methodology for monitoring AOPs was developed and assessed aiming to control and optimize these degradation processes. The effectiveness of FTIR to control the Fenton oxidation of phenol, which was used as a model compound, was tested, and its successful implementation led to establish the Fenton degradation mechanism of 1,4-dioxane, a target pollutant commonly found in industrial wastewater.

- An oxidation process may successfully be assessed by the newly developed methodology based on on-line FTIR, implying a significant reduction in the time devoted to analyses. The reaction intermediates that were produced during the Fenton oxidative degradation of phenol were fully assessed, and the mechanisms that were involved were also fully identified. The results obtained by FTIR were in total agreement with those obtained by chromatographic analyses.

- Thanks to receiving real-time information, this procedure allowed precise control of the effects of reagents on the treated substances, which furthermore enabled optimizing the quantities of reagents that were required in the process. This may further enable the successful optimization of the treatment combination of AOPs with biological technologies, reducing the cost of the treatment because the moment in the reaction where oxi-recalcitrant (but biodegradable) substances were mainly present in the solution was clearly identified.

- The FTIR probe allowed the identification of the main compounds involved in 1,4-dioxane's Fenton degradation; as well as the monitorization and optimization of the process aiming to determine the formation of biodegradable compounds, easily oxidizable by conventional biological treatments, hence saving chemical cost. A degradation mechanism was elucidated for the Fenton oxidation of 1,4-dioxane, which agreed with the proposal of Stefan and Bolton (1998) for the degradation pathway of 1,4-dioxane to form ethylene glycol mono- and diformate. However, ethylene glycol was identified in this case, and its mechanism of formation and degradation was proposed. These results contributed to clarify the degradation mechanism of 1,4-dioxane.

- The optimization of 1,4-dioxane's degradation using the Fenton process achieved the full removal of 1,4-dioxane, and an 80% CODs reduction under the best treatment conditions. The enhancement of wastewater's biodegradability was also obtained when a reduced amount of reagents

were used, which can be verified by the 51% increase of the content of volatile fatty acids. Although the total mineralization was not achieved, final products were more biodegradable than the initial 1,4-dioxane, therefore allowing a better efficiency of conventional biological treatment if the final requirements the wastewater should meet demands it.

- The application of the developed methodology to on-line control the treatment of industrial wastewater by AOPs has not been successful so far. Unfortunately, there is still the need for trying more sensitive on-line FTIR probes that could allow its use for monitoring industrial wastewater treatments.

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ORIGINAL PAPERS

PAPER I

D. Hermosilla, **N. Merayo**, A. Gascó, A. Blanco

The application of advanced oxidation technologies
to the treatment of effluents from the pulp and paper industry. A review

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Corresponding Author:	Daphne Hermosilla SPAIN
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Daphne Hermosilla
First Author Secondary Information:	
Order of Authors:	Daphne Hermosilla
	Merayo Noemi, Master
	Antonio Gascó, PhD
	Ángeles Blanco, PhD
Order of Authors Secondary Information:	
Abstract:	Paper industry is adopting zero liquid effluent technologies to reduce fresh water use and meet environmental regulations, which implies water circuits closure and the progressive accumulation of pollutants that must be removed before water re-use and final wastewater discharge. The traditional water treatment technologies that are used in paper mills (such as dissolve air flotation or biological treatment) are not able to remove recalcitrant contaminants. Therefore, advanced water treatment technologies, such as advanced oxidation processes (AOPs), are being included in industrial wastewater treatment chains aiming to either improve water biodegradability or its final quality. A deep review of the current state of the art regarding the use of advance oxidation treatments in the paper industry is herein addressed considering mature and emerging treatments for a sustainable water use in this sector. Wastewater composition, which is highly dependent of the raw materials being used in the mills, the selected AOP itself, and its combination with other water treatment technologies, will determine the viability of the treatment. In general, all advanced oxidation technologies have been reported to achieve good organics removal efficiencies. Particularly, ozonation has been the most widely reported and thoroughly assessed AOP at an industrial scale within pulp and paper mills, as it is also used as a bleaching treatment; whereas photo-Fenton and Fenton processes have resulted to be the most oxidative ones.
Suggested Reviewers:	Dieter Pauly RTD Strategy and Controlling, Papiertechnische Stiftung dieter.pauly@ptspaper.de He has a large experience in pulp and paper production and he has published numerous research manuscripts in this area.
	Yao Tung Lin National Chung Hsing University

	yaotung@nchu.edu.tw He has a large experience and a lot of manuscripts published in the AOPs' research area.
	Alenka Majcen University of Maribour alenka.majcen@um.si Her research interest is focused in AOPs and she has published numerous papers in this area.
Opposed Reviewers:	

The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry. A review

Daphne Hermosilla*[1], Noemí Merayo[1], Antonio Gascó[2], and Ángeles Blanco[1]

[1] Department of Chemical Engineering, Complutense University of Madrid. Ciudad Universitaria s/n, 28040 Madrid (Spain).

[2] IE University, School of Biology, Cardenal Zúñiga 12, 40003 Segovia (Spain).

*Corresponding author

Tel.: +34 91 394 4645.

E-mail: dhermosilla@quim.ucm.es

Abstract

Paper industry is adopting zero liquid effluent technologies to reduce fresh water use and meet environmental regulations, which implies water circuits closure and the progressive accumulation of pollutants that must be removed before water re-use and final wastewater discharge. The traditional water treatment technologies that are used in paper mills (such as dissolve air flotation or biological treatment) are not able to remove recalcitrant contaminants. Therefore, advanced water treatment technologies, such as advanced oxidation processes (AOPs), are being included in industrial wastewater treatment chains aiming to either improve water biodegradability or its final quality. A deep review of the current state of the art regarding the use of advance oxidation treatments in the paper industry is herein addressed considering mature and emerging treatments for a sustainable water use in this sector. Wastewater composition, which is highly dependent of the raw materials being used in the mills, the selected AOP itself, and its combination with other water treatment technologies, will determine the viability of the treatment. In general, all advanced oxidation technologies have been reported to achieve good organics removal efficiencies. Particularly, ozonation has been the most widely reported and thoroughly assessed AOP at an industrial scale within pulp and paper mills, as it is also used as a bleaching treatment; whereas photo-Fenton and Fenton processes have resulted to be the most oxidative ones.

Keywords: advanced oxidation processes; biodegradability; electro-oxidation; Fenton; ozone; paper industry; photocatalysis; wastewater treatment chains.

1. Introduction

Sustainable water use is a current concern within the pulp and paper industry, and great efforts are being made to minimize water consumption, as well as to reduce the environmental impact of final effluents. Therefore, global water use has been reduced from 600 m^3/T in 1974 to 4-100 m^3/T in modern paper mills, which has resulted in the progressive accumulation of pollutants in process water that must be removed to meet the quality standards required for water to be re-used or discharged (Ordóñez *et al.* 2014).

Pulp and paper mills generate a wide variety of pollutants to their effluents, depending on the implemented type of pulping process and the posterior pulp treatment (Pokhrel and Viraraghavan 2004). The main compounds present in virgin fiber pulp effluents are hemicelluloses, pectin, lipophilic extractives (such as resin acids), lignans, lignin-related substances, carbohydrates, and carboxylic acids (e.g. acetic and formic acids) in small quantities (Gullichsen and Fogelholm 1999; Sundholm 1999). In addition, chemical pulping processes have been reported to generate more than 40% low biodegradable organics within the total organic matter of the effluent (Dahlman *et al.* 1995); and particularly, sulphite processes also produce low biodegradable sulfonic compounds as by-products (Amat *et al.* 2004; Gregor *et al.* 1997).

On the other hand, effluents from recovered paper mills are different. The pH is not usually as strongly basic as for a kraft process, and more starch-related products (rather than lignin ones) can be found (Amat *et al.* 2005a), resulting that these effluents are more biodegradable (Merayo *et al.* 2013; Thompson *et al.* 2001). In addition, it is also important to consider that the papermaking operation with recycled fibers may introduce different chemical compounds in the effluent, such as EDTA, which is very difficult to degrade by biological technologies (Sundholm 1999). Other potential

contaminants that may be generated in the papermaking process are different process and product additives, such as fillers, whiteners, dyes, defoamers, dispersion agents, surfactants, biocides, and slimicides (Lacorte *et al.* 2003).

The concentrations of all these diverse compounds change along the different stages defined in the papermaking process. During pulping, most of the contaminants are released. During bleaching, residual lignin is removed to enhance brightness (Wang *et al.* 2004), and different chlorinated organic compounds can be generated in low proportions in Elemental Chlorine Free processes (Balcioglu *et al.* 2003; Yeber *et al.* 2007); whereas bleaching with alkaline hydrogen peroxide causes an additional load of 5-15 $Kg \cdot T^{-1}$ BOD_7 and 15-40 $kg \cdot T^{-1}$ COD, decreases hemicelluloses content, and increases the presence of pectin, lignin and aliphatic carboxylic acids. Alkalinity strongly influences the dissolution of hemicelluloses and pectin, and the release of dissolved and colloidal material (Sundholm 1999; Miranda and Blanco 2010).

Soluble biodegradable organic compounds may efficiently be removed by combinations of anaerobic and aerobic processes (Ordóñez *et al.* 2010), but these treatments do not prevent the accumulation of the non-biodegradable organic chemical fraction (Ahmad *et al.* 2007; Habets and Knelissen 1997), such as high molecular weight organics (>1000 Da) (Yeber *et al.* 2007), lignin and lignin-derived compounds (Chang *et al.* 2004; Dahlman *et al.* 1995; Eriksson and Kolar 1985; Thompson *et al.* 2001), toxic chlorinated organics (Balcioglu *et al.* 2007), and pollutants with sulfonic groups (Beltrán *et al.* 2000; Masuyama *et al.* 2000), among others. These chemicals usually produce alterations in the activity of biological reactors (Habets and Knelissen 1997). Furthermore, biological treatment may fail to remove color from pulp mill effluents (Balcioglu *et al.* 2007).

Therefore, the treatment strategy to reduce negative impacts from water circuits closure aims to remove high molecular weight (HMW) compounds, as well as some low molecular weight (LMW) recalcitrant organic matter (Bijan and Mohseni 2005). Considering biological treatment is not able to remove bio-recalcitrant compounds (Balcioglu *et al.* 2003; Bijan and Mohseni 2004), new trends are focused on incorporating other processes like advanced oxidation ones (AOPs) (Balabaniç *et al.* 2012; Balcioglu *et al.* 2003; Bijan and Mohseni 2004; Hermosilla *et al.* 2012). Particularly, Balabaniç *et al.* (2012) reported the removal of selected endocrine-disruptors from a recycled paper mill. Whereas the combination of biological treatments (anaerobic and aerobic) achieved about an 80% removal of different phtalates, photo-Fenton treatment achieved a 100% removal. In general, AOPs can be applied to industrial wastewater as a polishing step integrated with conventional chemical and/or biological processes in order to increase the overall treatment effectiveness (Alvares *et al.* 2001; Balcioglu *et al.* 2003; Legrini *et al.* 1993; Merayo *et al.* 2013; Oeller *et al.* 1997; Tanaka and Ichikawa 1993).

AOPs are based in the formation of hydroxyl radicals in sufficient quantity to effect the chemical transformation of contaminants (Glaze *et al.* 1987). It is known that hydroxyl radicals are almost twice as reactive as chlorine, and its oxidation potential is close to that of fluorine (E = 2.32 V/NHE at pH=7) (Bigda 1995). Highly reactive hydroxyl radical usually initiates the oxidative destruction of organic substances (R) present in wastewater by the following processes (Huang *et al.* 1993):

a) OH· addition reaction:

$$OH\cdot + R \rightarrow ROH\cdot \rightarrow \text{hydroxylated products} \qquad K \approx 10^{7}\text{-}10^{10}\ M^{-1}s^{-1} \qquad (1)$$

b) Hydrogen atom abstraction:

$$OH\cdot + R \rightarrow R\cdot + H_2O \rightarrow \text{oxidized products} \qquad K \approx 10^{7}\text{-}10^{10}\ M^{-1}s^{-1} \qquad (2)$$

Organic free radicals (R·) are formed as transient intermediates and are further oxidized by other intermediates to form stable, oxidized products (Huang *et al.* 1993).

The oxidation of phenolic compounds occurs more rapidly than non-phenolics one (Antunes *et al.* 2004). In the presence of electron-rich aromatic moieties, OH· preferentially reacts by addition (Antunes *et al.* 2004; Huang *et al.* 1993; Vieira and Steenken 1987). Phenoxyl radicals rapidly react with $O_2^{\bullet-}$ to produce aromatic ring-opening precursors of CO_2 (Antunes *et al.* 2004). On the other hand, aliphatic carboxylic acids are very stable, and their degradation rates by OH· are really low in the absence of UV light (Hermosilla *et al.* 2009b).

The ability of hydroxyl radical to break down the molecular structure of complex organic structures into simpler compounds has long been proven (Bigda 1995), and it has been shown successful for the partial oxidation of non-biodegradable organics such as lignin or chlorinated organics; therefore contributing to increase the biodegradability of the effluent as well (Balcioglu *et al.* 2003; Balcioglu *et al.* 2007; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Bijan and Mohseni 2008; Chang *et al.* 2004; Mansilla *et al.* 1997; Marco *et al.* 1997; Mounteer *et al.* 2007; Oeller *et al.* 1997; Salokannel *et al.* 2007; Yeber *et al.* 1999a; Yeber *et al.* 1999b). The full oxidation of organic compounds is however non-economically feasible because the use of large amounts of energy and chemicals would be necessary for achieving a complete mineralization (Bijan and Mohseni 2005).

The standalone use of AOPs for the treatment of pulp and paper mill effluents would mainly be limited by the fact they usually imply a high electrical energy demand or an excessive consumption of chemical reagents (Bauer and Fallmann 1997). Therefore, they will only be economically attractive if they are combined with other wastewater treatments (Mobius and Cordestolle 1997; Sarria *et al.* 2002). Moreover, the

use of AOPs as pre-treatment depends on wastewater composition. That is, effluents with high concentrations of hydroxyl radical scavengers (such as bicarbonate ions), or with a high presence of aliphatic carboxylic acids, which are difficult to be oxidized, will result in AOPs achieving lower degradation rates (Balcioglu and Cecen 1999; Barndõk *et al.* 2012; Gogate and Pandit 2004a; Gogate and Pandit 2004b).

In short, it is important to highlight that the application of AOPs within the pulp and paper industry has to be adapted to each particular case considering the influence of wastewater composition, the efficiency of the process itself, and the development of adequate procedures for the use of these technologies in mills with a very high degree of circuits closure, as well as the assessment of cost-effectiveness figures. A joint review of the application of AOPs to water treatment in the pulp and paper industrial sector is reported next.

2. Ozone oxidation processes

Ozone can oxidize other compounds in two different ways: directly reacting with dissolved substances; or indirectly, by hydroxyl radicals that are produced in its decomposition process (Esplugas *et al.* 2002). Due to the short half-life of ozone, continuous ozonation is required to keep the reaction going on. This is one of its major drawbacks, considering the high cost of generating ozone (Catalkaya and Kargi 2007; Kreetachat *et al.* 2007). Furthermore, the stability of ozone is also affected by the presence of salts (Barndõk *et al.* 2012), pH (alkaline solutions accelerate its decomposition generating hydroxyl radicals), and temperature (Bijan and Mohseni; Catalkaya and Kargi 2007); and process efficiency is highly dependent on an efficient gas liquid mass transfer, which is quite difficult to achieve due to the low solubility of ozone in aqueous solutions (Kreetachat *et al.* 2007).

Nevertheless, ozonation has successfully been used as a good method to oxidize chemicals present in wastewaters from pulp and paper mills, such as eugenol, cathecol, vainillin, guaiacol, syringaldehyde, phenol, chlorophenol, trichlorophenol, and cinnamic acid derivatives (Amat *et al.* 1999; Amat *et al.* 2005b; Fontanier *et al.* 2005a; Miranda *et al.* 2001). Particularly, Fontanier *et al.* (2005) reported the behavior of most of these organics in response to ozone treatment and described how the oxidation of phenol, chlorophenol and trichlorophenol takes place in one stage attributable to aromatic ring opening reactions; whether catechol, vanillin, guaiacol and syringaldehyde are oxidized in two stages due to the generation of intermediates that are more resistant to ozone attack. Oxidation proceeds by electrophilic attack, and then the reaction is favored when substituents with a donor effect are present. For example, trichlorophenol is highly reactive because chlorine atoms are weakly deactivating substituents and OH group is a very activating one, so these combining effects favor the electrophilic attack of ozone to the two free positions in the aromatic ring (Fontanier *et al.* 2005b).

On the other hand, the carboxylic acids that are formed by opening the aromatic ring have expectedly been reported to be very resistant to oxidation by ozone (Amat *et al.* 2003; Amat *et al.* 2005b; Bailey 1982; Balcioglu *et al.* 2007; Fontanier *et al.* 2005a; Hoigne and Bader 1983; Kreetachat *et al.* 2007), and they are usually responsible for TOC abatement limitation (Hoigne and Bader 1983); although they are generally highly biodegradable.

In addition, the ozone oxidation of resin acids has also been addressed relatively effective (Korhonen and Tuhkanen 2000; Laari *et al.* 2000; Ledakowicz *et al.* 2006; Roy-Arcand and Archibald 1996); whereas starch oxidation products showed lower degradation rates than lignin derivatives ones, probably due to the absence of carbon-carbon double bonds (Amat *et al.* 2005b; Langlais *et al.* 1991) (Figure 1). Furthermore,

why *p*-toluenesulfonic acid showed a slower degradation rate than other lignin derivatives was explained by the strong deactivating effect of its sulfonic group (Amat *et al.* 2004). In short, the composition of the pulp and paper industrial wastewater, which is mediated by the papermaking process itself, including raw materials and chemicals being used, is clearly determining the final oxidation treatment efficiency.

Particularly, the success of ozonation applied to real wastewater from pulp and paper mills, whether biologically pre-treated or not, and effluents from bleaching stages, has been mainly attributed to the effective degradation of toxic lignin products and chlorophenolic compounds (Amat *et al.* 2005b; Balcioglu *et al.* 2007; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Catalkaya and Kargi 2007; Fontanier *et al.* 2005b; Fontanier *et al.* 2006; Mansilla *et al.* 1997; Oeller *et al.* 1997; Rodríguez *et al.* 1998; Roy-Arcand and Archibald 1996; Salokannel *et al.* 2007; Sevimli 2005; Wang *et al.* 2004; Yeber *et al.* 1999a; Yeber *et al.* 1999b). As it has additionally been reported in several other essays, ozonation usually increases the biodegradability of paper mill effluents as well (Amat *et al.* 2005a; Balcioglu *et al.* 2007; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Fontanier *et al.* 2006; Helble *et al.* 1999; Mansilla *et al.* 1997; Nakamura *et al.* 1997; Oeller *et al.* 1997; Roy-Arcand and Archibald 1996; Salokannel *et al.* 2007); mainly because of the successful degradation of certain toxic compounds and the promoted changes in molecular weight fractions from HMW to LMW (Amat *et al.* 2005a; Balcioglu *et al.* 2007; Bauman and Lutz 1974; Fontanier *et al.* 2006; Hostachy *et al.* 1997; Mansilla *et al.* 1997). In fact, Amat *et al.* (2003) also reported that there is an optimum ozone dosage which allows achieving the maximum increase in biodegradability and the highest efficiency of an ozonation process. Further ozonation would have to progress oxidizing LMW carboxylic acids, but they did not show an enhanced biodegradability after this treatment. Summing up, the ozonation of paper mill

effluents aiming to increase biodegradability would only be advisable at a BOD_5/COD ratio < 0.2 (Oeller *et al.* 1997).

Color has particularly been reported to be removed very easily because its main responsible is the presence of lignin compounds, which double and triple bonds are easily oxidized by ozone (Bijan and Mohseni 2004; Joss *et al.* 2007; Kreetachat *et al.* 2007; Prat *et al.* 1989; Salokannel *et al.* 2007). In addition, and as it has just been pointed out, dechlorination of organochloride compounds is very effective; 60 minutes of reaction time have been reported enough to finish the breakdown of all organochlorides present in effluents from bleaching stages (chlorination, extraction and hypochlorite) of a pulp mill (Balcioglu *et al.* 2007). In summary, the results reported by different authors in terms of COD, TOC, color, and AOX removals, are very variable probably due to the diverse nature of the organics contained in the different treated effluents, whether they were biologically pre-treated or not, the mill of origin, or the diverse ozone feeding rates used in the treatments, although the average value resulted ≈40% (Figure 2). Particularly, Fontanier *et al.* (2005b) reported that some oxidized products by ozonation were transferred from the liquid to the solid phase in the presence of calcium salts, and its precipitation was subsequently produced. As a result, a 31% TOC removal was attributed to this phenomenon (Table 1).

Regarding the conditions under which ozonation was performed, several authors have reported that ozone resulted more effective in basic media (Amat *et al.* 2004; Amat *et al.* 2005b; Bijan and Mohseni 2005; Sevimli 2005; Wang *et al.* 2004), just as it was expected due to the more effective generation of hydroxyl radicals, which is a better oxidizing agent than molecular ozone (Bijan and Mohseni 2005; Glaze *et al.* 1987); although working under basic conditions also implies bearing with the presence of possible scavengers like carbonate or bicarbonate (Barndõk *et al.* 2012; Bijan and

Mohseni 2005). Putting it all together, no significant different treatment effectiveness was found between pH = 9 and 11 (Bijan and Mohseni 2005), but a significant lower treatment efficiency was addressed when pH was adjusted to neutral (Wang *et al.* 2004). Besides, Catalkaya and Kargi (2007) found a better degradation rate at pH = 9 than at 11, and also addressed that pH must be at least as low as 7 to perform an enhanced oxidation. Correspondingly, Medeiros *et al.* (2008) also showed higher color and HMW fraction removals and biodegradability increase at pH = 7 than at 12. More recently, Merayo *et al.* (2013) have reported non-significant differences between the ozone treatment of recycled paper mill effluents performed at pH = 7 and 12; and an even higher ozonation efficiency at pH = 7 for kraft pulp mill effluents. Considering all together, working at the typical pH values of neutral-basic pulp and paper mill effluents (pH = 7-9) addressed the great advantage of avoiding pH control mechanisms (Kreetachat *et al.* 2007; Oeller *et al.* 1997; Salokannel *et al.* 2007). Nevertheless, slight pH variations may occur during the oxidation reaction due to the formation of small acid by-products (Balcioglu *et al.* 2007; Merayo *et al.* 2013) or the generation of carbonate along the mineralization process (Oeller *et al.* 1997).

Regarding the temperature at which the process is performed, Salokannel *et al.* (2007) did not find differences from 21 to 35 ºC, although ozone transfer efficiency from gas to water was slightly lower at higher temperatures, implying an insignificant effect on reaction time. Accordingly, Bijan and Mohseni (2004) did not found significant differences in the ozonation efficiency of paper mill effluents from 20 to 60 ºC. Finally, Oeller *et al.* (1997) have also reported that increasing temperature did not provide any appreciable COD removal enhancement, although DOC removal resulted a 10-15% higher at 40 ºC and extended reaction times (> 90 minutes) than at 25 ºC, which furthermore implied consuming a higher O_3 amount as well.

Several authors have reported different insights considering the setup of an optimal ozone feeding rate. Initially, Bauman and Lutz (1974) and Nebel *et al.* (1974) proposed that the achieved oxidation does depend on the ozone feeding concentration in their early reports. On the other hand, Catalkaya and Kargi (2007) did not find color and TOC removals to be affected by ozone feeding rate working with effluents from paper mills, although AOX removal increased at higher ozone feeding rates. In fact, according to Salokannel *et al.* (2007), purification results are not expected to be influenced by the feeding gas ozone concentration; they rather depend on the ozone dose that is applied to water, and the feeding gas ozone concentration has a straight effect on the reaction time required to reach the desired ozone dose in water. Correspondingly, reaction rate is clearly dependent on ozone availability (Amat *et al.* 2004) and reaction time (Amat *et al.* 2003). Furthermore, in an enlightening work, Kreetachat *et al.* (2007) measured mass transfer to water when applying different ozone feeding rates, reporting that the volumetric mass transfer coefficient increases from 0.22 to 0.55 min^{-1} when the ozone feeding rate increases from 1 to 4 $L \cdot min^{-1}$, so the oxidation rate increases at a higher feeding rate because the driving force transferring ozone to the solution is greater.

Nevertheless, and as it has already been pointed out, ozone consumption rate will decrease during ozonation due to the progressive reaction with organic matter, so this decrease depends on the nature of the compounds present in the solution; that is, proportional to the amount of easily oxidized compounds (Fontanier *et al.* 2005b; Salokannel *et al.* 2007). Finally, Bierbaum and Oeller (2009) and Merayo *et al.* (2013) implemented on-line control systems for the continuous ozonation treatment of biologically treated effluents from recycled paper mills, showing that a controlled ozone production is useful and necessary, ensuring the stable operation of subsequent stages.

Controlling ozone on-line provided a 20% cost saving per year, resulting in an 8 month investment return for this type of systems.

In general, wastewater composition in terms of COD, TOC, AOX, and pH is insufficient to foresee the optimum operation conditions of ozone treatment because they would not be equivalent in different types of water since the structures of the organic compounds present in each one also significantly determine its oxidation success. Therefore, it is recommended to perform systematic laboratory tests with the scope of meeting the required target purification values in each case (Oeller *et al.* 1997).

2.1. Ozone oxidation plus biological treatment

The oxidation by ozone as a standalone technology may actually be considered as unfeasible for pulp and paper mill effluents, not offering sufficient removal and mineralization of organics (Bijan and Mohseni 2008) due to their usually high volume and a potential high content of biodegradable compounds in the solution after first ozonation stages. Furthermore, the oxidation of these effluents by ozone implies implementing large reactors and an excessive energy consumption; which may partially be overcome, even making ozonation economically feasible, using ozone oxidation to achieve the partial oxidation of the organic load enhancing the biodegradability of pulp and paper mill effluents (Alvares *et al.* 2001; Bijan and Mohseni 2004; Bijan and Mohseni 2005; Bijan and Mohseni 2008; Helble *et al.* 1999; Nakamura *et al.* 2004).

In fact, Bijan and Mohseni (2005) reported that whether a standalone biological or ozone treatment can reduce a 30% of the TOC mineralizing compounds of different nature, their combination improved TOC removal about a 20%. Considering all together the results found in the literature regarding the application of AOPs to pre or post biologically treated pulp and paper mill wastewater, an average 20-25% COD removal

enhancement is also addressed (Figure 3). Although biological post-treatment was more effective, differences to biological pre-AOP treatment were not statistically significant.

Other very interesting treatment alternative would consider first applying a biological or membrane treatment to separate the HMW fraction; therefore, the unnecessary oxidation of the LMW organic fraction is avoided. The concentrate from the membranes or the effluents from the biological treatment might then be ozonized, after which its biodegradability would be expected to improve highly back. Finally, a consequent more efficient second bio-treatment stage would be performed aiming to remove turbidity, color and COD (Bijan and Mohseni 2008; Manttari *et al.* 2008; Schlichter *et al.* 2003). Both combinations, Bio-O_3-Bio and NF-O_3-Bio, have been reported to result in similar final wastewater quality and ozone demand (Bijan and Mohseni 2008), that is, ≈40-50% mineralization, ≈60% COD removal, and an 80% color removal (Table 2); being ozone consumption 10 times lower than when ozonation without complementary pre- and post-treatments were performed. A more selective oxidation of HMW compounds and a more effective utilization of ozone were mainly addressed to drive such better results (Bijan and Mohseni 2008).

Besides, comparing both pre-treatments under real conditions, it results that membranes would produce lower rejection water volumes, so the ozone contactor may be reduced about a 50% in industry because the HMW fraction stream just constitutes the 45% of the total effluent (Bijan and Mohseni 2008). On the other hand, whether the integrated treatment with MBR and ozonation, whether the Bio-O_3-Bio system, both provided a considerable increase in COD reduction (Gommers *et al.* 2007; Merayo *et al.* 2013), but ozone use in the second alternative was more efficient than in the first one because the MBR effluent was made of components that resulted more difficult to be

chemically oxidized than in the case of using a continuous activated sludge (Gommers *et al.* 2007).

In addition, the use of bio-filters in combination with ozone has also been assessed, and results have shown that the combination of ozone with a subsequent bio-filter treatment required a lower amount of ozone to be supplied in the oxidation stage, as well as it would be ecologically preferable, reaching more than a 80% total COD removal (Helble *et al.* 1999; Mobius and Helble 2004).

Finally, Balcioglu *et al.* (2007) considered improving algal treatment with ozone pre-treatment. Overall efficiency mainly resulted enhanced in terms of color removal, but also significantly in COD and UV_{280}. Furthermore, the resident time of algal treatment was reduced from 8 to 5 days.

2.2. Combination of ozone and H_2O_2 in an oxidation treatment (peroxone)

The combination of ozone and hydrogen peroxide (O_3/H_2O_2) has also been proposed as a promising alternative to remove refractory organic chemicals (Masten and Davies 1994). According to Gogate and Pandit (2004), and Mounteer *et al.* (2007), H_2O_2 produces faster ozone degradation. In fact, a millimolar concentration of HO_2^- (the conjugate base of H_2O_2) initiates the decomposition of ozone also producing hydroxyl radical much more rapidly than hydroxide ion does (Catalkaya and Kargi 2007) as it is described by the following reactions (Glaze 1987):

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \quad (3)$$

$$HO_2^- + O_3 \rightarrow OH^\bullet + O_2^- + O_2 \quad (4)$$

In addition, ozone decomposition rate has been reported to increase at higher pH values because H_2O_2 dissociation into HO_2^- is favored (Catalkaya and Kargi 2007); so pH = 11 was addressed to be the most suitable value to perform this treatment. Besides,

it may be more adequate to perform the treatment at the normal pH values of the effluents from basic pulp and paper mills because the benefits of raising the pH may not compensate the cost of implementing and managing the required pH control system (Salokannel *et al.* 2007).

Although this combination may theoretically be more efficient than standalone ozone, results within the pulp and paper industry (Tables 1 and 2) did not always address this improvement when H_2O_2 was added to enhance ozone treatment. Particularly, Sevimli (2005) and Balabaniç *et al.* (2012) reported a 20% COD removal improvement when this treatment combination was applied to effluents from a biologically treated corrugated board factory and a recycled paper mill. In turn, Ko *et al.* (2009) reported an increase of color removal, but no effect on the reduction of the COD, when they treated diluted weak black liquor from a hardwood kraft pulp mill. In addition, Catalkaya and Kargi (2007) showed that peroxone treatment did not significantly improve the removal of both color and TOC (0.2% and 10%, respectively) from a biologically treated pulp mill effluent in comparison to the standalone use of ozone (Figure 2) adding 5 mM H_2O_2 at pH=11.

In fact, Mounteer *et al.* (2007) reported that the ozone dose had a greater effect on BOD behavior and on removing COD than the peroxide dose; but, the presence of H_2O_2 nevertheless had some beneficial effect increasing the average oxidation state. Finally, Salokannel *et al.* (2007) also reported that H_2O_2 did not add a noticeable effect on the removal of COD from a biologically treated effluent from a pulp and paper mill; probably because the reactions between molecular ozone and organic compounds competed with O_3/H_2O_2 reactions. Moreover, the improvement of biodegradability was also reported lower using O_3/H_2O_2 than standalone O_3 because the additional generation of radicals also degraded some biodegradable molecules.

According to these results, ozonation without the addition of H_2O_2 may also be considered a more reasonable treatment than the peroxone option from an economic point of view (Salokannel *et al.* 2007); although taking into account those trials reporting a significant treatment enhancement, it may depend on the characteristics of each effluent. Therefore a singular cost analysis should support the choice in any case.

2.3. Ozone/UV

In this treatment combination, the supplied UV energy interacts with O_3 as described in the following reaction (Beltrán *et al.* 1998; Esplugas *et al.* 2002; Guittonneau *et al.* 1990):

$$O_3 + H_2O \xrightarrow{hv} 2{\cdot}OH{\cdot} + O_2 \qquad (5)$$

But not all photo-assisted processes require the same light quality in terms of wavelength and energy to reach an optimal performance. Specifically, the direct photolysis of O_3 (and H_2O_2 as well) requires short-wavelength photons (<310 nm) (Hoffmann *et al.* 1995).

Particularly, the O_3/UV treatment combination showed a significant synergetic effect applied to starch degradation products. That is, COD removal increased from 3 to 24% when ozone treatment was photo-assisted at pH=6 (Amat *et al.* 2005b).In fact, these authors previously addressed that this synergetic treatment efficiency may only occur under acidic pH because ozone itself decomposes to OH· radicals under basic conditions, and irradiation would therefore be unnecessary (Amat *et al.* 2004). In addition, Ledakowicz *et al.* (2006) also reported that this treatment improved the removal of the COD from resin acids; results being particularly better at higher temperature (80 ºC).

Otherwise, non-significant differences in COD removal were addressed when this treatment was applied to actual pulp and paper industry effluents (Tables 1 and 2) due to its high turbidity; although the introduction of an ozone stream into the UV-photolysis system resulted in a significant improvement of both decolorization and dechlorination of paper mills effluents (Yeber *et al.* 1999b; Ledakowicz *et al.* 2006; Wang *et al.*).

In addition, O_3 consumption has been reported to be higher in the O_3/UV process than when O_3 was used standalone, resulting that a 90% additional O_3 was used to remove the COD (Oeller *et al.* 1997). Therefore, it was recommended to consider O_3 supply and UV radiation in any case and separately compare their results to its combination treatment in a single reactor chamber. In fact, Amat *et al.* (2005b) found a lower biodegradation improvement applying this treatment to an effluent from a cardboard mill than when it was treated with standalone ozone alone because of its higher aggressiveness producing more oxidized compounds; whereas Mansilla *et al.* (1997) and Wang *et al.* (2005) found similar results for both treatments applied to effluents from kraft pulp industry and chlorophenols, respectively.

Disparate results may be explained in terms of differences in the nature of the organic compounds contained in the treated solution. Molecular ozone is hardly able to attack highly deactivated aromatic rings (i.e. sulfonic compounds; (Amat *et al.* 2004) or highly oxidized LMW aliphatic carboxylic acids when it is the predominating oxidizing agent without applying irradiation; but it decomposes to produce hydroxyl radical ($OH\cdot$) when UV irradiation assists the process, which is a more powerful oxidation agent than ozone itself (Glaze *et al.* 1987). Therefore, more energy incises in the C-C bonds of organic molecules, which will be expected to be more easily oxidized. But for compounds that are actually more easily oxidizable, such as cinnamic acid derivatives

(Amat *et al.* 1999; Miranda *et al.* 2001), the synergistic effect between ozone and UV light is very low because they have more activated aromatic rings exposed to degradation, so molecular ozone is already able to attack them as efficiently as OH· does, and adding UV irradiance to the treatment producing the decomposition of ozone into OH· shows a very limited effect (Amat *et al.* 2004).

2.4. Catalytic ozonation

In the application of this treatment, ozone may react according to two possible pathways, corresponding to a direct reaction and the catalyzed process itself. Catalytic ozonation mainly provides the same advantages than the conventional one, but it significantly enhances organic matter removal and requires a much lower ozone dose (Fontanier *et al.* 2005b). Particularly, surface catalysis (heterogeneous) involves five consecutive steps which influence on the overall rate of the chemical conversion: (1) diffusion of the reagents towards the catalyst; (2) interaction of the reagents with the catalyst (adsorption); (3) reaction among the adsorbed reagents determining the products; (4) desorption of the products from the surface of the catalyst towards the medium; and (5) diffusion of the products away from the catalyst (Fontanier *et al.* 2006).

The almost complete mineralization of seven model compounds (phenol, chlorophenol, trichlorophenol, guaiacol, vanillin, catechol, and syringaldehyde) has been achieved using a catalyst containing cobalt as the active metal deposited on a mineral catalytic support (TOCCATAs-catalyzed ozonation; (Fontanier *et al.* 2005b), which are chemicals that have indeed also been reported to be easily oxidized by ozone. Furthermore, acetic acid resulted to be the most difficult final oxidation product to remove, such as it has also been addressed when applying Fenton, photo-Fenton, and

electro-Fenton processes to solutions containing different chemical moieties (Hermosilla *et al.* 2009b).

In addition, this treatment produced higher TOC removal figures than direct ozonation when applied to different effluents from paper mills (Fontanier *et al.* 2006). Pilot-scale trials reported a maximum removal of the 74% of the TOC and the 72% of the COD applying this treatment to different effluents of pulp mills; as well as the transformation of high molecular weight compounds into lower molecular weight ones was also addressed. Furthermore, a strong difference between the results of the application of this treatment to biologically treated effluents coming from mills using virgin or recycled fibers was clearly shown in this essay. When a biologically treated effluent from a recycled paper mill was treated, lower removal efficiency was achieved because the original wastewater composition was intrinsically more biodegradable (Table 2).

Another treatment alternative was proposed by Balcioglu *et al.* (2007) aiming to purify bleach effluents from a pulp mill using O_3 and granulated activated carbon (GAC) as catalyst. In this treatment, supplementary OH· radicals were formed thanks to the initiating role shown by activated carbon (Jans and Hoigne 1998). This system led to a COD removal improvement of the 23% with respect to direct ozonation; whereas it was just a 15% in comparison to standalone GAC. Higher AOX and color removals were also achieved. In addition, better COD and color removals were also reported treating diluted weak black liquor from a kraft pulp mill with ozone in the presence of activated carbon (Ko *et al.* 2009). This enhancement was primarily attributed to the regeneration of occupied sites on activated carbon. Moreover, the degradation of high molecular weight compounds was also reported higher than for simple ozonation (Balcioglu *et al.* 2007). Although both processes, ozonation and catalyzed ozonation,

enhanced toxicity removal, the treatment of bleach effluents combining O_3 and GAC significantly reduced the reaction time that was required to produce a non-toxic effluent. In fact, oxidation is more aggressive in catalyzed ozonation treatments than in standalone ozonation, so more oxidized compounds can be formed as treatment time runs on, and these may increase the toxicity of the effluent (Balcioglu *et al.* 2007).

In addition, the homogeneous catalytic ozonation of bleaching wastewater from a kraft pulp and paper mill increased COD removal up to about a 50-55% by the addition of 5 mM Fe^{2+} or Mn^{2+}; whereas it just resulted a 25% using standalone ozone (Balcioglu and Moral 2008). On the other hand, the treatment of the same wastewater with ozone combined with GAC resulted in a 63% COD removal (Table 2).

Finally, Mansilla *et al.* (1997) reported the capacity of the electron withdrawing ability of ozone to promote the generation of holes onto a catalyst surface. They applied an ozone photocatalytic treatment to effluents from a kraft pulp mill using ZnO as catalyst, achieving a 30% COD removal improvement in comparison to the application of standalone ozone. Complementarily, Yeber *et al.* (1999) reported that chloride ions were released to the solution, reaching maximum presence values after one minute of reaction time, when the treatment was performed with TiO_2; whereas for an O_3/UV/ZnO system, they reported this maximum chloride content after 15 minutes, thus showing a much slower efficiency on removing organochloride compounds.

3. UV Processes

An UV process is based on supplying energy to chemical compounds as radiation, which is absorbed by reactant molecules that are promoted to excited states and may further promote new reactions along treatment (Esplugas *et al.* 2002; Legrini *et al.* 1993). In general, UV alone is not considered as an effective treatment when applied

standalone in comparison to other AOPs (e.g. ozone (Amat *et al.* 2005b) or TiO_2/UV (Chang *et al.* 2004) (Table 3); although it may be more effective when combined with H_2O_2 (Ahmed *et al.* 2009), salts of particular metals (Fe), or ozone (see tables 2 and 3). Nevertheless, Catalkaya and Kargi (2007) determined that its best treatment efficiency would be achieved at pH = 3 when it is going to be applied to biologically pre-treated effluents from wood industry.

In particular, it has been demonstrated that radiation with a wavelength lower than 400 nm is able to photolize H_2O_2 molecules (Esplugas *et al.* 2002; Legrini *et al.* 1993). As a result, the addition of H_2O_2 to an UV treating system has been reported to significantly improve both color and TOC removals in comparison to a standalone UV treatment; even when low H_2O_2 concentrations were supplied (Catalkaya and Kargi 2007). On the other hand, Wang *et al.* (2004) assessed potential dechlorination of a bleaching kraft pulp mill effluent, finally reporting that the applied UV treatment did not achieve any significant removal (nor even color); and although the addition of H_2O_2 led to the removal of color, dechlorination did not further result improved. In addition, several authors have addressed the improvement of the process when it was performed at a basic pH, better if close to 11 (Ahmed *et al.* 2009; Catalkaya and Kargi 2007; Prat *et al.* 1988).

Nonetheless, even though COD and color reductions are improved in comparison to when H_2O_2 is used alone (Ahmed *et al.* 2009; Prat *et al.* 1988), the application of an H_2O_2/UV system is not generally economically competitive to other alternative processes because the achieved treatment improvement does not compensate the cost of implementing such technology (Prat *et al.* 1988). Particularly, although the color removal that would be achieved by the mere addition of H_2O_2 may be acceptable (≈30%) (Catalkaya and Kargi 2007; Joss *et al.* 2007), it has not enough power to induce

COD and TOC removals (<5%; (Catalkaya and Kargi 2007; Joss *et al.* 2007; Pérez *et al.* 2001), as it is reported in table 3.

4. Semi-conductor photocatalytic processes

These treatments imply the irradiation of a semiconductor (e.g. TiO_2, ZnO) with UV light at a wavelength shorter than 390 nm (Hoffmann *et al.* 1995; Yeber *et al.* 2000). The photoexcitation that is produced by UV light with an energy greater than the band gap is able to promote an electron from the valence band to the conduction band creating an electronic vacancy or "hole" (h^+) at the valence band edge; a process that can be simply represented by equation (6) for TiO_2, the most widely used semiconductor material in these processes (Antunes *et al.* 2004; Fujishim and Honda 1972).

$$TiO_2 \xrightarrow{2\ hv} TiO_2\ (2e^-, 2p^+) \qquad (6)$$

In order to perform a productive photocatalysis, electron-hole pair recombination must be suppressed (Antunes *et al.* 2004), which may be achieved by trapping either the photogenerated electron or the corresponding hole. Since the position of the valence band is very high for TiO_2 (3.1 V/SCE) (Fox 1989), the photogenerated hole will be able to oxidize a wide variety of organic substrates (S) to the corresponding radical cations (S^{+}), as it is expressed in the following equation (Antunes *et al.* 2004):

$$TiO_2(h^+) + S \rightarrow TiO_2 + S^{+} \qquad (7)$$

On the other hand, the photogenerated electron may instead be trapped by suitable acceptors (electron scavengers), being O_2 the most widely used one, forming the superoxide radical anion $O_2^{\bullet -}$ (Antunes *et al.* 2004; Fox 1989), as described by the next reaction:

$$TiO_2(e^-) + A \rightarrow TiO_2 + A^{\bullet -} \qquad (8)$$

It has been pointed out that TiO_2 is a more efficient catalyst than ZnO, respectively generating a 55% and a 31% TOC removals when mineralizing the organic matter of alkaline extractions from the bleaching sequence of a kraft pulp industry (Yeber *et al.* 2000) (Table 4). Better results with TiO_2 have also been reported by Kansal *et al.* (2008) treating acid effluents from a kraft/soda process that uses agricultural residues as raw material; whereas ZnO produced a higher COD removal in basic effluents. In addition, TiO_2 also resulted more efficient than ZnO when it was applied immobilized on glass (Yeber *et al.* 1999a). Finally, these essays also addressed that photocatalytic treatments performed with a supported catalyst resulted to be as efficient as when added in suspension. Although the supported type required longer reaction time to produce the same results (Yeber *et al.* 1999a; Yeber *et al.* 2000), it also allows the possibility of performing the treatment under flow conditions, thus avoiding the annoying catalyst recovering step that is required when the catalyst is added in suspension (Yeber *et al.* 2000), which otherwise represents a good advantage to take into account.

Catalyst doping has also been proposed in several essays to improve the efficiency of the process. Particularly, Mansilla *et al.* (1994) reported the use of a ZnO catalyst doped with Ag or Pt. The first one showed little effect on color and COD removals, whereas the second one induced modifications in the kinetic profile of color reduction (Table 4). In addition, Gouvea *et al.* (2000) reported the semiconductor-assisted photochemical degradation of lignin, dye, and kraft effluent using an Ag-doped ZnO catalyst. Results addressed that lignin color progressively decreased up to a 50% after 15 minutes of treatment; whereas it was almost total (99%) after 60 minutes.

The efficiency of the TiO_2-photocatalytic process, and therefore the required reaction time to maximize it, are influenced by the dosage of TiO_2 itself (Chang *et al.*

2004; Tanaka *et al.* 1999); that is, the degradation of organics is improved until an excessive catalyst dosage causes a shadow effect interfering with the transmission of UV light so the generation of electron-hole pairs cannot effectively occur (Catalkaya and Kargi 2008; Chang *et al.* 2004). Particularly, an optimum dosage of 10 $g \cdot L^{-1}$ of TiO_2 has been reported for the treatment of lignin powder, resulting in the 50% reduction of the color within the first 10 minutes of reaction (Chang *et al.* 2004); whereas the removal efficiencies of both color and DOC reached about a 90% when the process was extended up to 960 minutes.

In addition, although Catalkaya and Kargi (2008) reported good removal figures of organics (i.e. 80% TOC removal) by applying this treatment at basic pH to a biologically pretreated pulp and paper mill effluent, using 0.75 $g \cdot L^{-1}$ of TiO_2 at pH = 11 during 60 minutes (Table 4); working at a neutral pH produced better treatment efficiencies purifying effluents in a newsprint paper mill (Merayo *et al.* 2013), as well as it also yielded an almost complete decolorization of a kraft pulp mill effluent (Gouvea *et al.* 2000). A lower competition of anions and cations for the reactive sites of TiO_2 particles may be responsible for treatment improvement at neutral pH values. On the other hand, a 64% color removal was reported at pH = 7 for lignin decomposition, whereas a 99% was achieved at pH = 3 (Chang *et al.* 2004). Correspondingly, Boroski *et al.* (2008) and Rodrigues *et al.* (2008) also reported the highest efficiency of this process at pH = 3 (Table 4), which was attributed to the positive charge that TiO_2 surface acquire in acid solutions, which favors the adsorption of anionic compounds to be prioritized resulting in a great decolorization of the effluent (Yeber *et al.* 2007).

A rapid decrease of toxicity has also been reported for several effluents from the pulp and paper industry (Catalkaya and Kargi 2008; Chang *et al.* 2004; Pérez *et al.* 2001; Reyes *et al.* 1998; Yeber *et al.* 2000). Furthermore, COD was particularly

reported to be very efficiently removed (≈ 90%) from a bleaching effluent of a non-recovered paper mill by TiO_2 photocatalysis (Toor *et al.* 2007), and from an agro-residue-based soda bleaching effluent by both TiO_2 (COD removal ≈ 90%) and ZnO (COD removal ≈ 95%) photocatalytic treatments (Kansal *et al.* 2008) (Table 4). Virgin fiber was used in the pulping process, so its content in lignin, starch and resin acids surely contributed to a certain extent to these very successful results (Figure 1).

Finally, photocatalysis might be considered as an interesting alternative for pre- or post- biological treatment stages, as it has also previously been pointed out for ozonation (Merayo *et al.* 2013). For example, the relative quantity of HMW compounds considerably decreased (> 30%) in a kraft bleaching effluent that was subjected to supported photocatalytic treatments producing a higher content of LMW species in the solution (Yeber *et al.* 2000). In fact, the application of photocatalysis as post-biological treatment achieved a 75% color removal in the treatment of black liquor, which is 15 times higher than the resulting decolorization after a standalone photochemical process; as well as mineralization was enhanced up to a 140% with respect to the previous biological stage (Moraes *et al.* 2007). In addition, a 45% mineralization enhancement was also reported in this essay for the pre-biological treatment of kraft effluent by photocatalysis (Moraes *et al.* 2006) (Table 4).

4.1. Solar Photocatalysis

This process is based on the use of sunlight to provide the UV radiation that is required to be absorbed by the catalyst to perform the treatment. For example, Amat *et al.* (2005a) assessed its application to the treatment of effluents from board industry (recycle fibers) reporting good COD removal percentages, that is, about a 40% at pre-industrial level and a 50% in laboratory trials (Table 4); as well as Kansal *et al.* (2008)

addressed the solar photocatalytic treatment of bleaching effluent, reporting better results when using ZnO as catalyst than TiO_2, which is in contrast to the results previously reported using other UV light sources. Furthermore, the achieved chemical degradation resulted faster than when using other UV light sources.

Otherwise, Amat *et al.* (2005) reported that COD removal resulted lower than when applying a solar photo-Fenton treatment (Tables 4 and 5); which agrees with the essay performed by Gomathi and Kanmani (2006). In both essays, the degradation of organics was mainly driven towards the pollutants that are more reluctant to biological degradation. In addition, better results were addressed for derivatives from lignin than for non-aromatic compounds. That is, whereas the treatment of eugenol by solar photocatalysis resulted in a 60% COD removal, a 30% was just reached treating guaiacol. Furthermore, 27% COD removal was addressed for *p*-toluenesulfonic acidic solutions; and only aliphatic LMW carboxylic acids (e.g. maleic, oxalic, and formic acids) were found as by-products of the process. Finally, the application of this treatment to acidic fractions resulting from starch degradation led to similar COD removal figures (≈ 20%) to those addressed by ozone/UV and photo-Fenton processes. As it has already been pointed out, these compounds are more reluctant to be treated by AOPs because of the inherent lower reactivity of C-C bonds in comparison to C=C ones (Amat *et al.* 2005a).

The combination of solar photocatalysis and biological treatment has also recently been assessed for effluents from chlorination and the alkaline extraction of soda pulp bleaching stages in an agro-residue-based pulp and paper mill using ZnO as catalyst (Dhir *et al.* 2012). In summary, this treatment achieved a 53% COD removal treating the chlorinated effluent, and a 43% when it was applied to the alkaline-extracted one; whereas the overall treatment efficiency reached a 92% COD removal

when solar ZnO-photocatalysis was applied to the chlorinated effluent as the pre-treatment of a biological process, and it resulted 95% when it was combined as the post-treatment of the biological degradation of the alkaline extracted effluent (Table 4)

4.2. UV/TiO_2/H_2O_2

Several essays have considered the addition of hydrogen peroxide to the UV/TiO_2-photocatalytic treatment in order to assess the potential generation of hydroxyl radicals as an additional oxidizing agent. All these trials reported COD removal improvements in comparison to a regular UV/TiO_2 treatment (Catalkaya and Kargi 2008; Chang *et al.* 2004; Kumar *et al.* ; Muñoz *et al.* 2006; Pérez *et al.* 2001; Rodrigues *et al.* 2008), particularly when performed at a pH value close to neutral. Two possible roles have been proposed for the action of H_2O_2 (Pérez *et al.* 2001): (a) being an alternative electron acceptor to oxygen at the conductance band, or (b) accepting electrons from the superoxide anion; as expressed by the following equations:

(a) $e^-_{CB} + H_2O_2 \rightarrow OH\cdot + OH^-$ (9)

(b) $O_2^{\bullet-} + H_2O_2 \rightarrow OH\cdot + OH^- + O_2$ (10)

Particularly, this treatment led to a 50% COD removal after 6 h of irradiation when it was applied to an ECF effluent of a pulp mill, and a 50% TOC removal was finally achieved after 7 h of treatment (Pérez *et al.* 2001); Table 4). Therefore, COD removal can be mainly attributed to organic matter mineralization. On the other hand, Rodrigues *et al.* (2008) reported that the addition of H_2O_2 to an UV/TiO_2 treatment did not significantly improve degradation rate, but increased the velocity of the photo-process in the treatment of cellulose and paper industry effluents; although Boroski *et al.* (2008) did report a higher increase of the degradation results produced by the photocatalytic process adding H_2O_2 along the treatment of the same type of effluent

(Table 4). In addition, the better performance of this treatment was also addressed by Kumar *et al.* (2011), who reported a 10% increase of the COD removal when H_2O_2 was added to the treatment of a non-recovered paper mill effluent by TiO_2-photocatalysis (Table 4).

Furthermore, Balcioglu *et al.* (2003) reported a 40% COD removal (Table 4) when treating kraft bleaching effluents by this treatment; as well as chloride release and an increase of the BOD_5/COD ratio were also addressed. Additionally, Catalkaya and Kargi (2008) achieved an 84% TOC removal applying this treatment to pre-biologically treated effluents from the pulp and paper industry (Table 4); and Mounteer *et al.* (2007) further reported the increase of organic matter content in the treated effluent after performing this type of treatment, which might have been caused by colloidal matter solubilization during the oxidative process. In short, about an average 10% COD removal enhancement could be expected when the photocatalytic treatment of pulp and paper mill effluents is assisted by the addition of H_2O_2 (Figure 2).

4.3. UV/TiO_2/O_2

In this aeroxide process, oxygen is used as an efficient electron trap preventing electrons to return back to photo-generated holes. Mansilla *et al.* (1997) addressed the application of this treatment to effluents from kraft pulp industry reporting a 50% COD removal; whereas Yeber *et al.* (1999b) assessed a 50% toxicity abatement in cellulose mill effluents from bleaching sequences (Table 4). In addition, this essay also showed a slight better treatment efficiency when TiO_2 was used as catalyst in the O_2-assisted photocatalytic treatment of these effluents in comparison to using ZnO as catalyst, or in combination with O_3 (Tables 2 and 4). In fact, better mineralization rates were obtained using TiO_2 photocatalytic systems rather than applying ZnO catalyzed ones.

Furthermore, Yeber *et al.* (2007) reported the removal of 70% of the COD, 50% TOC, 94% color, and 50% toxicity, when applying this treatment to effluents from the first extraction step of ECF bleaching pulp (Table 4). Finally, applying either UV/TiO_2/O_2 or UV/ZnO/O_2 processes to an effluent from a bleaching sequence, Yeber *et al.* (1999b) also reported the release of chloride ions to the solution, which maximum content was detected after five minutes of treatment.

4.4. UV/TiO_2/Cu (II)

Biodegradation efficiency might also be improved using metallic ions as electron acceptors, as proposed by Yeber *et al.* (2007) in the same essay the aeroxide treatment just described was also assessed. In short, it was confirmed that copper (II) efficiently acted as an electron acceptor when photocatalytic treatment was applied to an ECF bleaching pulp effluent to which this metallic ion was added. Therefore, this should be considered a very interesting treatment alternative for effluents that are contaminated with both organic matter and metal ions because the use of additional oxygen is avoided (Yeber *et al.* 2007). The removal of 70% of the COD, 50% TOC, and 50% toxicity was also achieved performing this photocatalytic treatment type (Table 4).

5. Fenton processes

Fenton process is based on the electron transfer between H_2O_2 and Fe^{2+}, which acts as an homogenous catalyst, to produce hydroxyl radical (OH·), which is able to powerfully degrade organic compounds, as it is expressed by the following equation (Harber and Weiss 1934):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad K_1 = 70.0\ M^{-1}\cdot s^{-1} \qquad (11)$$

The highly reactive hydroxyl radical that is produced along the Fenton process initiate the oxidative destruction of organic substances typically present in wastewater according to equations 1 and 2 (Huang *et al.* 1993). The iron cycle implying Fe^{2+} and Fe^{3+} forms plays the catalyst role according to the following reactions (Pignatello *et al.* 2006):

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO^{\cdot}_2 + H^+ \qquad K_2 <<< K_1 \qquad (12)$$

$$H_2O_2 + OH^{\cdot} \longrightarrow HO^{\cdot}_2 + H_2O \qquad K_3 = 3.3 \cdot 10^7\ M^{-1} \cdot s^{-1} \qquad (13)$$

$$Fe^{2+} + OH^{\cdot} \longrightarrow Fe^{3+} + OH^- \qquad K_4 = 3.2 \cdot 10^8\ M^{-1} \cdot s^{-1} \qquad (14)$$

$$Fe^{3+} + HO^{\cdot}_2 \longrightarrow Fe^{2+} + O_2H^+ \qquad K_5 < 2.0 \cdot 10^3\ M^{-1} \cdot s^{-1} \qquad (15)$$

$$Fe^{2+} + HO^{\cdot}_2 + H^+ \longrightarrow Fe^{3+} + H_2O_2 \qquad K_6 = 1.20 \cdot 10^6\ M^{-1} \cdot s^{-1} \qquad (16)$$

$$HO^{\cdot}_2 + HO^{\cdot}_2 \longrightarrow H_2O_2 + O_2 \qquad K_7 = 8.3 \cdot 10^5\ M^{-1} \cdot s^{-1} \qquad (17)$$

$$HO^{\cdot}_2 + H_2O_2 \longrightarrow OH^{\cdot} + H_2O + O_2 \qquad K_8 = 3.0\ M^{-1} \cdot s^{-1} \qquad (18)$$

Although it has been addressed that the optimal pH value to perform this treatment is about 3.0 (e.g. Tambosi *et al.* 2006; Kazmi and Thul 2007) it has also been indicated that it was really better performed at a pH value ranging from 5.0 to 6.0. due to the final coagulation of iron hydroxides, which further favors COD and color removals (Catalkaya and Kargi 2007; Tambosi *et al.* 2006). In fact, performing this treatment at more basic initial pH implies avoiding pH-control operation and cost, and the process itself tends to produce acids that lower the pH to more efficient acidic values anyway. Regarding this chance, good treatment efficiencies have already been addressed performing this treatment under natural initial neutral pH conditions (Hermosilla *et al.* 2012), although the best removal results were always achieved at pH = 2.8.

In general, Fenton processes have produced better overall results treating pulp and paper mill effluents than other AOPs-based treatment technologies (Figure 2). Particularly, a 95% COD removal was reported for the Fenton treatment of synthetic black liquor wastewater optimizing the treatment by central composite experimental design (Torrades *et al.* 2011). Similarly, the treatment of reverse osmosis concentrate flowing out a specific pilot treatment train implemented in a recycled paper mill, consisting of anaerobic and aerobic biological stages followed by ultrafiltration and reverse osmosis membrane treatments, was also tested and optimized by surface response methodology by Hermosilla *et al.* (2012), and an 80% COD removal was achieved at the best resulting treatment conditions (Table 5).

In addition, Sevimli (2005) reported that color was effectively eliminated by this treatment method from pulp industry effluents that were biologically pre-treated; as well as it was proven the superiority of this process to more effectively remove refractory organics (COD removal = 83%; Table 5) than O_3 (COD removal = 43%; Table 1) and O_3/H_2O_2 (COD removal = 64%; Table 2) processes. In addition, it is also a more economic AOPs-based treatment alternative (Hermosilla *et al.* 2012). Correspondingly, Catalkaya and Kargi (2007) reported the removal of an 85% of the color and an 88% of the TOC; whereas Kazmi and Thul (2007) achieved a 98% color removal and a 62% COD reduction; both applying Fenton treatment to biologically pre-treated pulp and paper mill effluents (Table 5).

Nevertheless, despite this treatment process is generally more oxidative than other alternatives non-considering the assistance of radiation as well, Amat *et al.* (2005a) only addressed a 3% COD removal for the treatment of acid fractions from starch degradation, which was attributed to the inherent organic structure of these compounds. Furthermore, Pirkanniemi *et al.* (2007) tested Fenton treatment for the

particular removal of EDTA from ECF bleaching effluent, concluding that it could be used as an effective pre-treatment prior to its biological treatment.

Finally, Tambosi *et al.* (2006) assessed the applicability of a so-called Fenton-like reaction, consisting in initiating the Fenton process with Fe (III) instead of Fe (II), to treat a paper mill wastewater. Maximum COD removals ranging from 30 to 50% were reported depending on the supplied hydrogen peroxide and Fe^{3+} dosages, and nearly 100% of color and aromatic compounds were removed as well (Table 5). Despite addressing these good results, the partially oxidized composition of the treated wastewater showed a higher acute toxicity to *Artemia salina* than the untreated effluent.

5.1. Photo-Fenton

The use of UV light in combination with Fenton's reagent, that is, the so-called photo-Fenton process, is able to re-generate ferrous iron reducing ferric ions and producing additional hydroxyl radical content by photolysis according to the following equation (Faust and Hoigne 1990; Kavitha and Palanivelu 2004; Kim and Vogelpohl 1998):

$$Fe(III)OH^{2+} + h\nu \rightarrow Fe^{2+} + OH\cdot \quad (20)$$

Besides, the photo-decarboxylation of ferric carboxylates is also produced as expressed by the following equations (Kavitha and Palanivelu 2004; Safarzadeh-Amiri *et al.* 1996):

$$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R\cdot \quad (21)$$

$$R\cdot + O_2 \rightarrow RO\cdot_2 \rightarrow \text{Products} \quad (22)$$

As a result, the amount of catalytic iron that would be required to produce the same treatment results, and the volume of sludge consequently generated, could be strongly reduced; as well as some additional organic compounds (carboxylates) that are very difficult to treat by AOPs may otherwise be effectively treated by this

methodology (Hermosilla *et al.* 2009a; Hermosilla *et al.* 2009b). Consequently, the photo-Fenton alternative has generally been shown to be more efficient in the degradation of effluent components than its dark version (Karimi *et al.* 2010), and improves both the total quantity and the rate of TOC abatement in comparison to the UV/H_2O_2 system (Catalkaya and Kargi 2007; Hermosilla *et al.* 2009b; Hermosilla *et al.* 2012).

Considering those factors affecting the process, the influence of irradiation wavelength on the treatment depends on the catalyst that would be used. Whereas photons with a wavelength close to 400 nm are required to successfully perform a standard photo-Fenton process using ferrous iron as catalyst; the absorption of photons is preferred at 550 nm in Fenton-like processes that are based on Fe(III)/H_2O_2 mixtures (Pignatello *et al.* 1999; Sun and Pignatello 1993).

In addition, the temperature dependence of this process has also been assessed addressing the result of an improved reaction rate when temperature was raised from 25 to 40 ºC (Pérez *et al.* 2002b). Therefore, temperature seems to be assisting alternative ways of H_2O_2 cleavage, OH· formation, or Fe (II) recovery. On the other hand, the same persistent organic fraction (TOC = 50 ppm) remained in solution from 40 to 70 ºC; and bubbling O_2 through the solutions neither improved the results of this treatment (Pérez *et al.* 2002b).

Furthermore, although Catalkaya and Kargi (2007) considered an initial pH=5-6 to be better to perform Fenton treatment in wastewater from pulp and paper industry; it is important highlighting negligible amounts of iron hydroxides are expected to be generated in a photo-Fenton process, and pH will always evolve towards the optimal more acid value along the process (e.g. Tambosi *et al.* 2006). In fact, faster TOC removal rates have been shown at pH=2.8 (Hermosilla *et al.* 2009a; Pérez *et al.* 2002b).

Besides, either a strong acidic media (pH=1.5), or under neutral-basic conditions (pH=8) slowed down the process mainly because of the instability that hydrogen peroxide and iron species showed in the solution (Hermosilla *et al.* 2012).

And finally, it is important to take into account in processes that involve both iron presence and UV light irradiation that the quantum yield of light absorption by Fe(III) directly depends on the specific absorbing iron species. $Fe(OH)^{2+}(H_2O)_5$ is the predominant species at pH=2-3, and it holds one of the largest light absorption coefficients and quantum yields for $OH\cdot$ production along with Fe (II) regeneration, ranging from 280 to 370 nm (Benkelberg and Warneck 1995; Pérez *et al.* 2002b).

Regarding the particular performance of this treatment within the paper industry, the removal of 85% of the TOC, 82% color, and 93% AOX content was achieved (Table 5) adding 50 mM of H_2O_2 and 2.5 mM of Fe(II) and applying 5 minutes of UV irradiation to a pulp mill effluent (Catalkaya and Kargi 2007). In addition, Pérez *et al.* (2002) reported a TOC reduction of about 60%, and the total removal of LMW chlorinated compounds (Table 5), after 30 min of UV irradiation assisting a Fenton treatment of 450 ppm of Fe(II) and 7500 ppm of H_2O_2 being applied to purify an effluent from the chlorinated step of the bleaching sequence of a kraft pulp mill.

Complementarily, Justino *et al.* (2011) assessed the assistance of the photo-Fenton treatment with fungi (*Rhizopus oryzae* and *Pleurotus sajor caju*), and an enzyme (laccase) aiming to remove individual phenols from a bleached kraft pulp and paper mill final effluent that had previously undergone secondary treatment. The complete removal of phenols was addressed when *Rhizopus oryzae* and photo-Fenton oxidation were combined (Table 5) whereas with *P. sajor caju* and laccase just achieved a 60-85% removal. In line with these results, Hermosilla *et al.* (2012) also reported the photo-

Fenton treatment as being able to totally remove the organic load present in the concentrate from a reverse osmosis installed in a recycled paper mill (Table 5).

Finally, ultrasonic irradiation and a Fenton-like treatment just provided a 12% COD removal when they were applied to bleaching effluents from pulp and paper mills (Table 5); and although the photo-Fenton oxidation treatment using Fe (III) degraded up to the 84-93% of some model compounds of wood extractives, it only reached to removed 20% of the COD after 30 minutes of treatment (Eskelinen *et al.* 2010). These poor results removing COD were probably caused by the inherent neutral pH value that is characteristic of this wastewater (pH=6.9), which has recently been reported as non-optimal to perform this process, and it has also been proved to be of greater relevance than for performing dark Fenton (Hermosilla *et al.* 2012).

6.2. Solar photo-Fenton

Photo-Fenton processes can alternatively be driven by low-energy photons in the visible range of the spectrum (Pérez *et al.* 2002b; Safarzadeh-Amiri *et al.* 1996). As a result, photo-Fenton processes may be implemented at a significantly reduced cost when performed using solar irradiation (Pérez *et al.* 2002b). As it has already been pointed out, the optimal treatment would be performed at pH=2.8, which is related to iron speciation in the solution (Hermosilla *et al.* 2009b; Pérez *et al.* 2002a; Torrades *et al.* 2003). Besides, a good TOC removal (> 60%) has also been achieved treating bleaching effluent at an initial pH value of 6, adding the advantage of avoiding the extra operation and cost associated to initial pH adjustment (Xu *et al.* 2007); as well as better treatment results were reported at 50ºC than at a lower treatment temperature in this essay. Correspondingly, Torrades *et al.* (2003) also reported a 35% TOC removal increase

when solar photo-Fenton treatment was applied to a kraft pulp mill effluent at a right temperature interval ranging from 30 to 45-60 ºC.

In particular, approximately a 60 and a 30% COD removals were obtained applying this treatment to solutions containing eugenol and guaiacol (lignin derivatives), respectively (Amat *et al.* 2005a). These authors also effectively treated *p*-toluenesulfonic solutions by solar photo Fenton, achieving a 47% degradation of this compound. In addition, a 40% of the residual sulphur was determined as sulphate, that is, the final solution enhanced its biodegradability. Furthermore, they reported a 24% COD removal after 7 hours of solar irradiation in the treatment of a simulation of the acidic fraction from starch degradation (sodium acetate 2.5 $g \cdot L^{-1}$, sodium butyrate 2.5 $g \cdot L^{-1}$ and glucose 2.5 $g \cdot L^{-1}$); whereas only a 3% COD removal was achieved by the dark process.

Considering the specific application of solar photo-Fenton to pulp and paper effluents (Table 5), Torrades *et al.* (2003) particularly addressed a 60% TOC removal and the total elimination of LMW chlorinated compounds that were initially present in kraft bleaching effluents applying 30 min of irradiation using 450 ppm of Fe(II) and 7500 ppm of H_2O_2. Moreover, Xu *et al.* (2007) also reported an almost 70% TOC removal when treating a recycled pulp and paper mill effluent by solar photo-Fenton for 3 hours. Additionally, Amat *et al.* (2005) achieved a 23-50% COD removal in board industry effluents (recycled fibers) depending on the composition of the sample, which better explained the reported differences in wastewater treatment efficiency rather than concentration.

Finally, very good particular COD removal results (90% after a 2h-process) have been reported in the treatment of biologically pre-treated pulp and paper mill wastewater. This improvement may be attributed to the previous removal of

biodegradable material in the biological stages of the treatment train; whereas directly treating the raw wastewater mixture of contaminants would have reduced the efficiency of the solar photo-Fenton process because certain oxidative power would have been lost trying to degrade biodegradable, but recalcitrant to oxidation, organic compounds.

6. Electro-oxidation Processes

Electrochemical oxidation is based on the direct degradation of organic compounds on the electrodes, the generation of hydroxyl and other oxidative radicals by wastewater electrolysis, and the action of other by-products generated during the process. Current density applied during treatment, electrode material, reaction time, and the characteristics of the wastewater to be treated are the main factors affecting this treatment process. Perng *et al.* (2008) particularly assessed the influence of pH reporting better results at higher values; that is, the treatment at pH = 9 (hydraulic retention time = 57 s, electrode gap = 15 mm, and current density = 287 $A \cdot m^{-2}$) of an effluent from a paper mill producing corrugating medium resulted in a 28% COD removal and a 94% color removal (Table 5).

In particular, the electro-oxidation treatment of kraft bagasse bleaching effluent applying a current density of 0.87 $A \cdot dm^{-2}$ during 1.75 h reported a 53% COD removal (Antony and Natesan 2012); whereas a 63% reduction of the COD was achieved in a cellulose pulp mill effluent that was treated applying 22.5 $A \cdot dm^{-2}$ during 180 minutes (Buzzini *et al.* 2006) (Table 5).

Furthermore, the combination of electro-oxidation with a post-biological treatment stage of the same kraft bagasse bleaching effluent increased the overall COD removal up to an 87% (Antony and Natesan 2012). The synergistic effect of these combined treatments was attributed to the produced increase of the biodegradability of

the effluent after the electro-oxidation step. Moreover, the combination of electro-coagulation (1 $A \cdot dm^2$ during 34.4 minutes), electro-oxidation (1.5 $A \cdot dm^2$ during 90.5 minutes), and biological process (521 minutes) applied to the same wastewater addressed a 95% COD removal; and the operating cost resulted lower indeed (Antony and Natesan 2012).

In addition, the treatment of model compounds from the paper industry even addressed better results. For example, the electrochemical oxidation of lignosulfonate achieved an 80% TOC removal (Domínguez-Ramos *et al.* 2008). Moreover, the treatment of lignin obtained from Saiccor's acid bisulphite-based pulping process resulted in the production of vanillin, which would be a byproduct of interesting commercial value (Moodley *et al.* 2011).

Finally, the combination of Fenton process with electrochemical oxidation (namely, electro-Fenton treatment) is a further interesting alternative. Its application to a biologically-treated newsprint paper industry effluent addressed a 95% color removal and a 90% COD reduction (Selvabharathi and Kanmani 2010) (Table 5). As previously reported for other Fenton processes, performing the treatment at higher pH values decreased the efficiency because of the precipitation of $Fe(OH)_3$ (Selvabharathi and Kanmani 2010).

7. Oxone™ (Peroxymonosulfate salt; $2KHSO_5$:$KHSO_4$:K_2SO_4)

Joss *et al.* (2007) assessed the treatment performance of this commercial salt aiming decolorization of an alkaline stage effluent from a kraft pulp mill. Oxone™ mainly resulted effective during the initial phases of the treatment. A 5 $g \cdot L^{-1}$ Oxone™ treatment produced a 79% color removal, a 14% COD reduction, and a negligible TOC abatement

(Table 5). The adjustment of the pH was not necessary because this salt performs treatment over a wide range of values.

Conclusions

AOPs are a promising alternative to develop new treatment strategies in the paper industry aiming to either improve water reuse or fulfill the legislation in force regarding wastewater discharge. In fact, several AOPs-based treatment possibilities have already been assessed successful for pulp and paper industry wastewater at a laboratory scale in many cases. In particular, ozonation has received further attention due to the possibility of using already available facilities for this treatment in some mills previously devoting them for bleaching.

The composition of wastewater is one of the main factors affecting the final efficiency of the application of AOPs-based treatments to effluents from the pulp and paper industry; particularly resulting more efficient when lignin compounds are highly present in wastewater from virgin fiber mills.

Considering together all the results that have been reported for the application of AOPs to effluents of the pulp and paper industry it comes out that standalone ozonation achieved the worst treatment efficiency figures (COD removal ≈ 40%). Fenton processes addressed the best ones (COD removal ≈ 70%), and photocatalysis showed an intermediate performance (COD removal ≈ 50%).

Furthermore, it has especially been addressed that the combination of AOPs with biological stages generally enhances overall treatment efficiency and reduces its cost. Although differences were not assessed significant, using AOPs as a post-biological treatment has specifically been reported as a more efficient alternative.

In short, the use of AOPs within pulp and paper mills is conditioned by the nature of wastewater composition, the efficiency of the process itself, and its potential combination with other treatment technologies to newly implement, or already existing within the facilities of the mill; as well as the assessment of final economic figures.

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Table 1. Ozone oxidation treatment results for paper industry effluents.

Effluent type	Removal (%)	COD	TOC	Color	AOX	DBO_5/COD improvement	Reference
Cardboard industry, recycled paper		38					(Amat *et al.* 2005b)
CEH bleaching effluent, wood		23		74	46	Yes	(Balcioglu *et al.* 2007)
Kraft bleach effluent, wood		25				Yes	(Balcioglu and Moral 2008)
Biologically treated, recycled		51					(Bierbaum and Oeller 2009)
Alkaline bleach effluent, wood				70		Yes	(Bijan and Mohseni 2004)
Kraft bleach effluent, wood		21	20	70		Yes	(Bijan and Mohseni 2005)
Kraft ECF effluent, wood		17	5			Yes	(Bijan and Mohseni 2008)
Biologically treated, wood			29	91	62		(Catalkaya and Kargi 2007)
Biologically treated, wood		97	[a]98	100			(Fontanier *et al.* 2005b)
Biologically treated, wood		52	39				(Fontanier *et al.* 2006)
Biologically treated, recycled		36	19				(Fontanier *et al.* 2006)
Biologically treated bleached sulphate pulp, wood		76	51				(Fontanier *et al.* 2006)
Biologically treated		40					(Gommers *et al.* 2007)
Final discharge		55					(Hostachy *et al.* 1997)
Kraft Eop effluent, wood		18	14	74		No	(Joss *et al.* 2007)
Kraft weak black liquor, hardwood		58		85			(Ko *et al.* 2009)
Wood			24	85			(Kreetachat *et al.* 2007)
Kraft bleach, wood		20		30		Yes	(Mansilla *et al.* 1997)
Biologically treated mechanical pulp mill and board mill effluent, mixture		20		65		Yes	(Manttari *et al.* 2008)
Alkaline bleach effluent, wood		16	0	62			(Medeiros *et al.* 2008)
Kraft E1 effluent, wood			5	27			(Moraes *et al.* 2006)
Diluted black liquor, wood			0	14			(Moraes *et al.* 2006)
Kraft bleach effluent, wood		4	7	8	10		(Morais *et al.* 2008)
Kraft bleach effluent, wood			[b]47				(Muñoz *et al.* 2006)
Biologically treated, recycled (75%) and wood (25%)		80	[b]47				(Oeller *et al.* 1997)
Partly biologically treated, recycled		20	[b]22				(Oeller *et al.* 1997)
Biologically treated, recycled		85	[b]31				(Oeller *et al.* 1997)
Biologically treated, wood		82	[b]64				(Oeller *et al.* 1997)
Biologically treated, recycled		53	[b]18				(Oeller *et al.* 1997)
Partly biologically treated, recycled		41	[b]18				(Oeller *et al.* 1997)
Biologically pretreated, wood		12	[b]9	50	25	Yes	(Salokannel *et al.* 2007)
Biologically pretreated, wood		18	[b]9	85	25	Yes	(Salokannel *et al.* 2007)

Biologically treated, recycled	43	91		(Sevimli 2005)
ECF bleach effluent, birch wood	40			(Tuhkanen *et al.* 1997)
ECF bleach effluent, pine wood	23			(Tuhkanen *et al.* 1997)
Kraft ECF effluent, wood		72	Yes	(Yeber *et al.* 1999b)
Newsprint, recycled	40			(Merayo *et al.* 2013)
Kraft effluent, wood	57			(Merayo *et al.* 2013)
Newsprint biologically treated, recycled	38			(Balabaniç *et al.* 2012)

[a] 31 % TOC removal due to precipitation.
[b] DOC

Table 2. The combination of ozone oxidation with other treatment technologies within the pulp and paper industry.

Effluent type	Treatment	Removal (%) COD	TOC	Color	AOX	DBO_5/COD improvement	Reference
CEH bleaching, wood	O_3 + algal	90		99	87		(Balcioglu *et al.* 2007)
Alkaline bleach, wood	O_3 + Bio		50				(Bijan and Mohseni 2005)
ECF, wood	O_3 + Bio	57	40				(Bijan and Mohseni 2008)
ECF, wood	Bio + O_3 + Bio	58	50	80			(Bijan and Mohseni 2008)
ECF, wood	NF + O_3 + Bio	65	40	80			(Bijan and Mohseni 2008)
Biologically treated, woodfree	O_3+biofilter	81					(Helble *et al.* 1999)
Biologically treated, recycled	O_3+biofilter	57					(Helble *et al.* 1999)
Newsprint, recycled	Bio + O_3	90					(Merayo *et al.* 2013)
Newsprint, recycled	O_3 + Bio	81					(Merayo *et al.* 2013)
Paper industry, wood	O_3+biofilter	60					(Mobius and Helble 2004)
Paper industry, wood	O_3+biofilter+O_3+biofilter	85					(Mobius and Helble 2004)
ECF, wood	O_3 + Bio	58					(Yeber *et al.* 1999b)
ECF, wood	O_3/UV + Bio	63					(Yeber *et al.* 1999b)
ECF, wood	O_3/UV/TiO_2 + Bio	70					(Yeber *et al.* 1999b)
ECF, wood	O_3/UV/ZnO + Bio	62					(Yeber *et al.* 1999b)
Newsprint biologically treated, recycled	O_3/H_2O_2	59					(Balabaniç *et al*. 2012)
Biologically treated, wood	O_3/H_2O_2		31	81	95		(Catalkaya and Kargi 2007)
Kraft weak black liquor, hardwood	O_3/H_2O_2	50		90			(Ko *et al.* 2009)
ECF, wood	O_3/H_2O_2	20	5	67		Yes	(Mounteer *et al.* 2007)
Biologically treated, wood	O_3/H_2O_2	10		82	35	Yes	(Salokannel *et al.* 2007)
Biologically treated, paper mill	O_3/H_2O_2			90	35	Yes	(Salokannel *et al.* 2007)
Biologically treated, recycled	O_3/H_2O_2	64		97			(Sevimli 2005)
Cardboard industry, recycled paper	O_3/UV	42					(Amat *et al.* 2005b)
Kraft pulp, conventional bleaching, wood	O_3/UV	20		40		Yes	(Mansilla *et al.* 1997)
Kraft bleach effluent, wood	O_3/UV		[a]68				(Muñoz *et al.* 2006)
Biologically treated, 90% recycled, 10% TMP	O_3/UV	14	[a]5				(Oeller *et al.* 1997)
Bleaching (CEPDD), wood	O_3/UV			72			(Wang *et al.* 2004)
ECF, wood	O_3/UV		76			Yes	(Yeber *et al.* 1999b)
Kraft pulp, conventional bleaching, wood	O_3/UV/ZnO	52		40		Yes	(Mansilla *et al.* 1997)
Bleaching (CEPDD), wood	O_3/UV/H_2O_2			76			(Wang *et al.* 2004)
ECF, wood	O_3/UV/ZnO	44	70			Yes	(Yeber *et al.* 1999b)

ECF, wood	O_3/UV/TiO_2	51	72			Yes	(Yeber *et al.* 1999b)
CEH bleaching, wood	O_3/Active carbon	46		87	80	Yes	(Balcioglu *et al.* 2007)
Kraft bleach effluent, wood	O_3/Active carbon	63				Yes	(Balcioglu and Moral 2008)
Kraft bleach effluent, wood	O_3/Fe^{2+}	52				Yes	(Balcioglu and Moral 2008)
Kraft bleach effluent, wood	O_3/Mn^{2+}	53				Yes	(Balcioglu and Moral 2008)
Biologically treated, wood	Catalytic ozonation	84	84	100			(Fontanier *et al.* 2005b)
Biologically treated, wood	Catalytic O_3, continuous mode	75	61	95			(Fontanier *et al.* 2005b)
Biologically treated, wood	Catalytic ozonation	67	74				(Fontanier *et al.* 2006)
Biologically treated, recycled	Catalytic ozonation	53	35				(Fontanier *et al.* 2006)
Biologically treated, bleached sulphate pulp, wood	Catalytic ozonation	72	73				(Fontanier *et al.* 2006)
Kraft weak black liquor, hardwood	O_3/Active carbon	60		88			(Ko *et al.* 2009)
Kraft weak black liquor, hardwood	O_3/Active carbon/H_2O_2	65		95			(Ko *et al.* 2009)

[a]DOC

Table 3. Hydrogen peroxide and UV treatments applied to effluents from the pulp and paper industry.

Effluent	Treatment	Removal (%)	COD	TOC	Color	AOX	Reference
Pulp and paper mill, wood	H_2O_2		10				(Ahmed *et al.* 2009)
Biologically treated, wood	H_2O_2			5	24	34	(Catalkaya and Kargi 2007)
Kraft Eop effluent, wood	H_2O_2		1	0	31		(Joss *et al.* 2007)
Pulp and paper mill, wood	UV		0.3				(Ahmed *et al.* 2009)
Biologically treated, wood	UV			4	7	17	(Catalkaya and Kargi 2007)
Kraft (CEPDD) effluent, wood	UV				6		(Wang *et al.* 2004)
Pulp and paper mill, wood	UV/H_2O_2		92	90			(Ahmed *et al.* 2009)
Biologically treated, wood	UV/H_2O_2			11	41	19	(Catalkaya and Kargi 2007)
Biologically treated, wood	UV/H_2O_2			45			(Catalkaya and Kargi 2008)
Kraft ECF filtrate, wood	UV/H_2O_2		0	0	30		(Mounteer *et al.* 2007)
Coagulated-flocculated bleaching effluent, wood	UV/H_2O_2		37				(Rodrigues *et al.* 2008)
Kraft bleach effluent, wood	UV/H_2O_2					100	(Ugurlu and Karaoglu 2009)
Kraft (CEPDD) effluent, wood	UV/H_2O_2				67		(Wang *et al.* 2004)

Table 4. Photocatalytic treatments application to effluents from the pulp and paper industry.

Effluent	Treatment	Removal (%)	COD	TOC	Color	AOX	DBO_5/COD improvement	Reference
Newsprint biologically treated, recycled	TiO_2/UV		39					(Balabaniç *et al.* 2012)
Biologically treated, wood	TiO_2/UV			80				(Catalkaya and Kargi 2008)
RO concentrate newsprint, recycled	TiO_2/UV		35	30				(Hermosilla *et al.* 2012)
Kraft/soda bleach effluent, agricultural residual materials	TiO_2/UV		88					(Kansal *et al.* 2008)
Pulp and paper mill effluent, hardwood	TiO_2/UV		54		84			(Kumar *et al.* 2011)
Newsprint, recycled	TiO_2/UV		20					(Merayo *et al.* 2013)
Kraft bleach effluent, wood	TiO_2/UV			[a]15				(Muñoz *et al.* 2006)
Bleach effluent, wood	TiO_2/UV		89					(Toor *et al.* 2007)
Kraft ECF effluent, wood	TiO_2/UV		16			71		(*Pérez et al.* 2001)
Coagulated-flocculated bleaching effluent, wood	TiO_2/UV		40					(Rodrigues *et al.* 2008)
Agro-residue-based soda bleaching effluent	ZnO/UV		55					(Dhir *et al.* 2012)
Kraft/soda bleach effluent, agricultural residual materials	ZnO/UV		94					(Kansal *et al.* 2008)
Diluted black liquor, wood	ZnO/UV		57		80			(Mansilla *et al.* 1994)
Kraft E1 effluent, wood	ZnO/UV			15	54			(Moraes *et al.* 2006)
Diluted black liquor, wood	ZnO/UV			0	5			(Moraes *et al.* 2006)
Kraft ECF effluent, wood	TiO_2/UV/H_2O_2 supported				40			(Mounteer *et al.* 2007)
Kraft alkaline extraction conventional bleaching, wood	TiO_2/UV/O_2 supported		58	55		90		(Yeber *et al.* 1999a)
Kraft ECF effluent, wood	TiO_2/UV/O_2 supported + Bio		70				Yes	(Yeber *et al.* 1999a)
Kraft alkaline extraction conventional bleaching, wood	TiO_2/UV supported		58	55		90		(Yeber *et al.* 2000)
Kraft alkaline extraction conventional bleaching, wood	ZnO/UV supported		58	31		90		(Yeber *et al.* 2000)
Kraft alkaline extraction conventional bleaching, wood	ZnO/UV/O_2 supported		58	31		90		(Yeber *et al.* 1999a)
Kraft ECF effluent, wood	ZnO/UV/O_2 supported		44				Yes	(Yeber *et al.* 1999a)
Diluted black liquor, wood	Pt-ZnO/UV		57		80			(Mansilla *et al.* 1994)
Kraft effluent, wood	Ag-ZnO/UV			15	99			(Gouvea *et al.* 2000)
Agro-residue-based soda bleaching effluent	ZnO/solar UV + Bio		93	89				(Dhir *et al.* 2012)
Agro-residue-based soda bleaching effluent	Bio + ZnO/solar UV		86					(Dhir *et al.* 2012)

Newsprint, recycled	Solar TiO_2 + Bio	83					(Merayo *et al.* 2013)
Newsprint, recycled	Bio + solar TiO_2	82					(Merayo *et al.* 2013)
Kraft E1 effluent, wood	ZnO/UV + Bio		62				(Moraes *et al.* 2006)
Diluted black liquor, wood	ZnO/UV + Bio		36				(Moraes *et al.* 2006)
Kraft ECF effluent, wood	ZnO/UV/O_2 + Bio	64					(Yeber *et al.* 1999b)
Board industry, recycled	TiO_2/solar UV	40					(Amat *et al.* 2005a)
Biologically treated effluent	TiO_2/solar UV	83					(Gomathi and Kanmani 2006)
Kraft/soda bleach effluent, agricultural residual materials	TiO_2/solar UV	61					(Kansal *et al.* 2008)
Agro-residue-based soda bleaching effluent	ZnO/solar UV	53					(Dhir *et al.* 2012)
Kraft/soda bleach effluent, agricultural residual materials	ZnO/solar UV	74					(Kansal *et al.* 2008)
Kraft Bleaching, wood	TiO_2/UV/H_2O_2	40				Yes	(Balcioglu *et al.* 2003)
Kraft Bleaching, wood	TiO_2/UV/H_2O_2	51				Yes	(Balcioglu *et al.* 2003)
Electrocoagulated-flotated bleaching effluent, wood	TiO_2/UV/H_2O_2	64				Yes	(Boroski *et al.* 2008)
Biologically treated, wood	TiO_2/UV/H_2O_2		84				(Catalkaya and Kargi 2008)
Pulp and paper mill effluent, hardwood	TiO_2/UV/H_2O_2	65		89			(Kumar *et al.* 2011)
Kraft bleach effluent, wood	TiO_2/UV/H_2O_2		[a]22				(Muñoz *et al.* 2006)
Kraft ECF effluent, wood	TiO_2/UV/H_2O_2	50	50		90		(*Pérez et al.* 2001)
Coagulated-flocculated bleaching effluent, wood	TiO_2/UV/H_2O_2	55					(Rodrigues *et al.* 2008)
Kraft bleach effluent, wood	TiO_2/UV/H_2O_2				91		(Ugurlu and Karaoglu 2009)
Kraft alkaline extraction conventional bleaching, wood	TiO_2/UV/O_2	50		40		Yes	(Mansilla *et al.* 1997)
Kraft ECF effluent, wood	TiO_2/UV/O_2	53	72			Yes	(Yeber *et al.* 1999b)
Kraft ECF effluent, wood	TiO_2/UV/O_2 + Bio	67					(Yeber *et al.* 1999b)
Kraft first extraction effluent ECF, wood	TiO_2/UV/O_2	70	50	94		Yes	(Yeber *et al.* 2007)
Kraft alkaline extraction conventional bleaching, wood	ZnO/UV/O_2	57		42		Yes	(Mansilla *et al.* 1997)
Kraft ECF effluent, wood	ZnO/UV/O_2	51	70			Yes	(Yeber *et al.* 1999b)
Kraft first extraction effluent ECF, wood	TiO_2/UV/Cu	70		94		Yes	(Yeber *et al.* 2007)

[a] DOC

Table 5. Fenton processes and Oxone™ treatment results for effluents from the pulp and paper industry.

Effluent	Treatment	Removal (%)	COD	TOC	Color	AOX	Phenols	Reference
Newsprint biologically treated, recycled	Fenton		75					(Balabaniç *et al.* 2012)
Biologically treated, wood	Fenton			88	85	89		(Catalkaya and Kargi 2007)
RO concentrate newsprint, recycled	Fenton		80					(Hermosilla *et al.* 2012)
Chemimecanical pulp effluent, wood	Fenton				20			(Karimi *et al.* 2010)
Soda bagase pulp effluent, wood	Fenton				62			(Karimi *et al.* 2010)
Biologically treated, pulp and paper mill	Fenton		62		98			(Kazmi and Thul 2007)
Kraft Chlorination step, wood	Fenton			40	>90			(*Pérez et al.* 2002b)
Biologically treated, recycled	Fenton		83		95			(Sevimli 2005)
Equalization tank paper mill	Fenton-like		50		100			(Tambosi *et al.* 2006)
Equalization tank paper mill	Fenton-like pilot scale		52	90	98			(Tambosi *et al.* 2006)
Biologically treated, wood	photo-Fenton			85	82	93		(Catalkaya and Kargi 2007)
Bleach effluent, wood	photo-Fenton		20					(Eskelinen *et al.* 2010)
RO concentrate newsprint, recycled	photo-Fenton		100					(Hermosilla *et al.* 2012)
Biologically treated kraft ECF effluent, wood	photo-Fenton						100	(Justino *et al.* 2011)
Chemimecanical pulp effluent, wood	photo-Fenton				41			(Karimi *et al.* 2010)
Soda bagase pulp effluent, wood	photo-Fenton				65			(Karimi *et al.* 2010)
Kraft bleach effluent, wood	photo-Fenton			[a]30				(Muñoz *et al.* 2006)
Kraft bleach effluent, wood	photo-Fenton		67		91			(Pereira *et al.* 2009)
Kraft bleach effluent, wood	photo-Fenton		85		81			(Pereira *et al.* 2009)
Kraft Chlorination step, wood	photo-Fenton			60	>90			(*Pérez et al.* 2002b)
Newsprint biologically treated, recycled	photo-Fenton		96					(*Balabaniç et al.* 2010)
Bleach effluent, wood	Fenton-like + ultrasonic		12					(Eskelinen *et al.* 2010)
Kraft bleach effluent, wood	photo-Fenton/TiO_2			30				(Muñoz *et al.* 2006)
Board industry, recycled	solar photo-Fenton		50					(Amat *et al.* 2005a)
Biologically treated effluent	solar photo-Fenton		90					(Gomathi and Kanmani 2006)
Kraft bleaching effluent (22% ClO_2 substitution), wood	solar photo-Fenton			60				(Torrades *et al.* 2003)
Bleaching effluent (H_2O_2), wood	solar photo-Fenton			70				(Xu *et al.* 2007)
Kraft bagasse bleaching effluent	Electro-oxidation		53					(Antony and Natesan 2012)
Biologically treated, cellulose	Electro-oxidation		63	38	96			(Buzzini *et al.* 2006)
Corrugating medium mill effluent, recycled	Electro-oxidation		28		94			(Perng *et al.* 2008)

Kraft bagasse bleaching effluent	Electro-oxidation + bio	87			(Antony and Natesan 2012)
Kraft bagasse bleaching effluent	Electro-coagulation+ electro-oxidation+bio	95			(Antony and Natesan 2012)
Biologically treated effluent	Electro-Fenton	90		95	(Selvabharathi and Kanmani 2010)
Kraft EOP effluent, wood	Oxone™ [b]	14	0	79	(Joss *et al.* 2007)

[a] DOC

[b] Peroxymonosulfate salt

Figure 1. COD removal by AOPs in the pulp and paper industry considering the type of fiber (recycled or virgin fiber - wood), and comparison to the treatment of resin acids (resin), starch degradation products (starch), and lignin. Letters (a, b) identify different statistically significant groups by Tukey's test, $P < 0.05$).

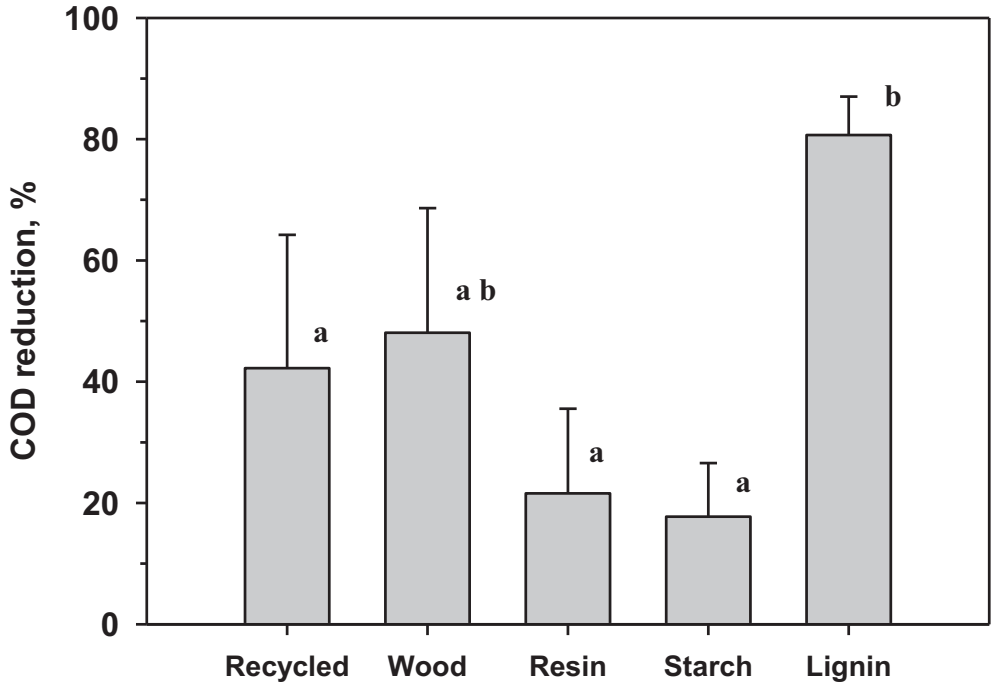


Figure 2. COD removal by AOPs in the pulp and paper industry (Ozone+ includes all treatment combinations with ozone. TiO_2+ includes non-supported $TiO_2/UV/H_2O_2$ treatments. Letters (a, b) label different statistically significant groups identified by Tukey's test, $P < 0.05$).

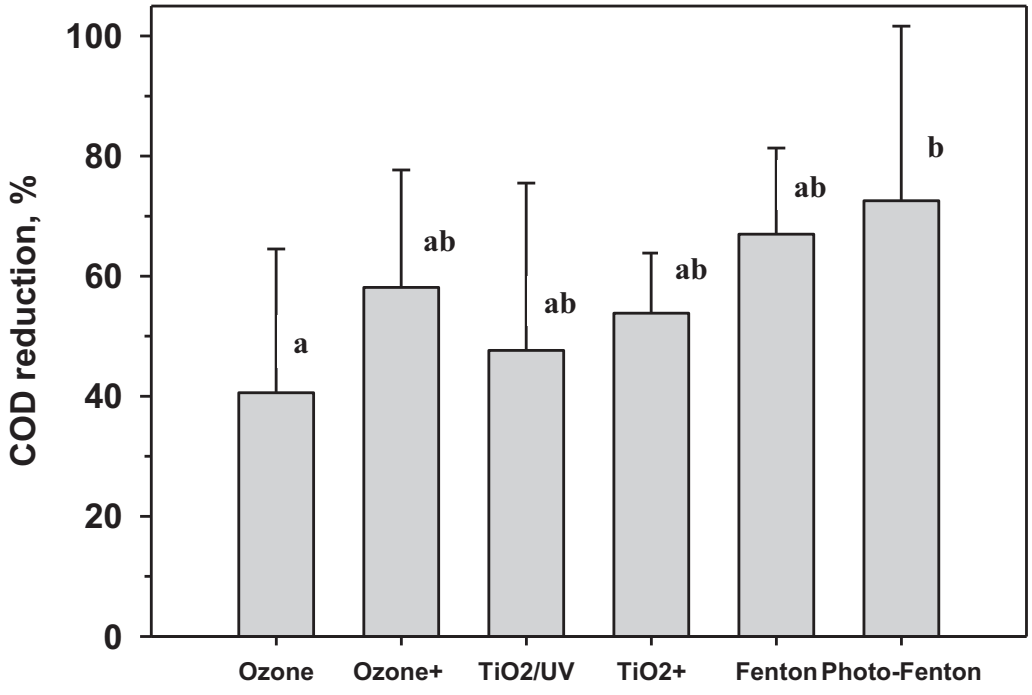
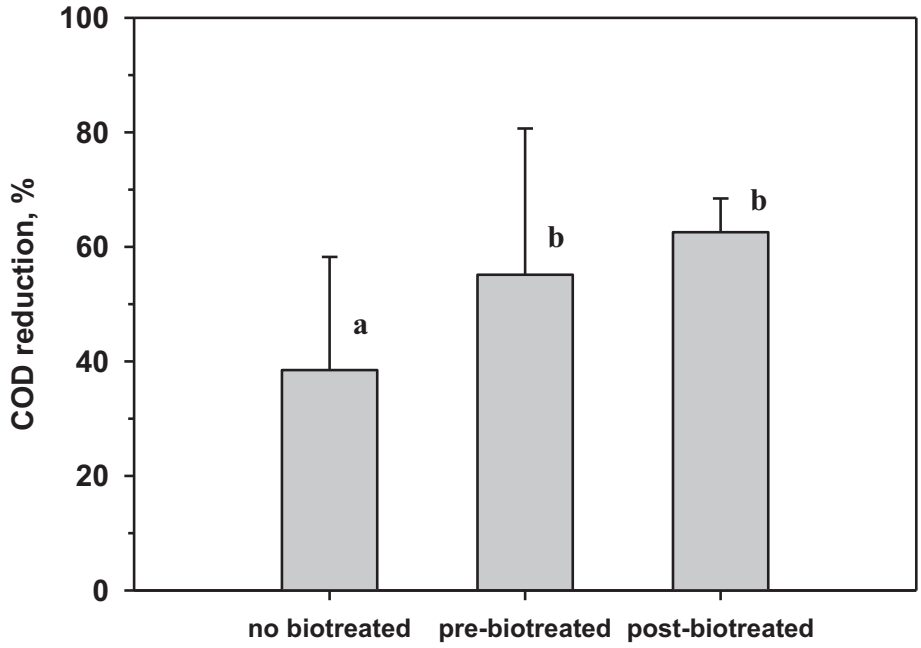


Figure 3. COD removal by AOPs combined with biological treatment (Letters (a,b) identify statistically significant groups by Tukey's test, $P < 0.05$).



PAPER II

N. Merayo, D. Hermosilla, L. Blanco, L. Cortijo, A. Blanco

Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry

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Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry

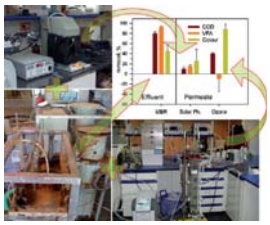
Noemí Merayo, Daphne Hermosilla*, Laura Blanco, Luis Cortijo, Ángeles Blanco

Department of Chemical Engineering, Complutense University of Madrid, Facultad de Ciencias Químicas, Ciudad Universitaria s/n, 28040 Madrid, Spain

HIGHLIGHTS

- 2.4 g O_3 L^{-1} achieved about a 60% COD removal treating a kraft pulp mill effluent.
- 10 g TiO_2 L^{-1} produced a COD removal <30% treating pulp and paper effluents.
- The composition of pulp and paper mill's effluents influenced its AOPs treatment.
- AOPs as pre-biological treatment did not result in significant better results.
- Very good COD and colour removals (>90%) were achieved combining MBR + ozonation.

GRAPHICAL ABSTRACT



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ABSTRACT

The closure of water circuits within pulp and paper mills has resulted in a higher contamination load of the final mill effluent, which must consequently be further treated in many cases to meet the standards imposed by the legislation in force. Different treatment strategies based on advanced oxidation processes (ozonation and TiO_2-photocatalysis), and their combination with biological treatment (MBR), are herein assessed for effluents of a recycled paper mill and a kraft pulp mill. Ozone treatment achieved the highest efficiency of all. The consumption of 2.4 g O_3 L^{-1} resulted in about a 60% COD reduction treating the effluent from the kraft pulp mill at an initial pH = 7; although it only reached about a 35% COD removal for the effluent of the recycled paper mill. Otherwise, photocatalysis achieved about a 20–30% reduction of the COD for both type of effluents. In addition, the effluent from the recycled paper mill showed a higher biodegradability, so combinations of these AOPs with biological treatment were tested. As a result, photocatalysis did not report any significant COD reduction improvement whether being performed as pre- or post-treatment of the biological process; whereas the use of ozonation as post-biological treatment enhanced COD removal a further 10%, summing up a total 90% reduction of the COD for the combined treatment, as well as it also supposed an increase of the presence of volatile fatty acids, which might ultimately enable the resultant wastewater to be recirculated back to further biological treatment.

1. Introduction

Despite the great efforts made by the paper industry to close its water circuits, it still remains the second largest sector demanding water use [1]. Therefore, further challenges should still be

* Corresponding author. Tel.: +34 91 394 4645; fax: +34 91 394 4243.
E-mail address: dhermosilla@quim.ucm.es (D. Hermosilla).

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faced up in order to keep meeting current standards related to the quantity and quality of discharged wastewater [2], and developing innovative technologies for reusing and/or recycling wastewater within the process in order to minimize the environmental impact of pulp and paper mills. Totally closing water circuits using current available technologies may lead to significant trouble in the process, as well as other problems related to water quality requirements. Therefore, new treatment strategies should aim to remove biodegradable high molecular weight (HMW) organic compounds, as well as low molecular weight (LMW) recalcitrant organic matter [3].

In particular, new trends are focussed on incorporating alternative treatment types like advanced oxidation processes (AOPs), which may be able to remove recalcitrant compounds [4,5]. In fact, AOPs have already been applied to industrial wastewater as a polishing step integrated with conventional chemical and/or biological processes in order to increase overall treatment efficiency [4,6]. Furthermore, the application of AOPs to pulp and paper mill effluents might only be economically attractive in combination to other wastewater treatment type [7], particularly considering they usually imply a high demand of energy, or an excessive reagents consumption [8].

Moreover, the use of AOPs within pulp and paper mills should take into account the influence of wastewater composition on its potential treatment. Pulp industry effluents, such as those outflowing from wood chemical pulping processes, generate more than a 40% low biodegradable organics within the total organic matter content present in the final effluent [9]. On the other hand, effluents from paper mills using recovered paper as raw material are rather characterized by the presence of biodegradable starch-related products than by their content of lignin compounds [10]. In addition, it is also important to consider the efficiency of the process itself and the development of adequate protocols for using these processes in mills with a high degree of circuits closure [11]; as well as take into good account its economical assessment.

Ozonating wastewater from pulp and paper mills has been previously reported to remove colour very easily because its main responsible is the presence of lignin compounds, which double and triple bonds were easily oxidized by ozone [5,12]. In addition, ozonation has also been reported to increase the biodegradability of effluents from pulp and paper mills, mainly because of the degradation of toxic compounds, and the promoted changes in the molecular weight fractions (from HMW to LMW) [1,13].

Complementarily, the application of TiO_2-photocatalytic treatment within the pulp and paper industry has previously been reported to show an efficient reduction of colour and dissolved organic carbon when heterogeneous TiO_2-photocatalytic processes have been applied to different types of effluents and lignin-containing solutions; as well as a rapid decrease of their toxicity and biodegradability improvement have also been addressed [14–17].

In short, ozonation and photocatalysis have not usually been considered as feasible treatments to be used standalone because of the large amounts of chemicals and energy that they require for its proper performance; but their combination with biological processes may increase the overall treatment efficiency [3,18], therefore enhancing their viability.

Among available biological technologies, membrane biological reactors (MBR) involve important advantages over other more conventional biological processes, namely: a superior resulting effluent quality, higher control of solids and hydraulic retention time, and smaller installation volume and footprint [19]. As a consequence, they have previously been considered for enhancing sustainable water reuse within paper mills [20]; moreover if a final reverse osmosis step is required [21].

A comparative essay is herewith reported considering two very different effluents from pulp and paper industry (a kraft pulp mill, and a 100% recycled paper mill effluents) in order to assess the influence of wastewater composition on AOPs efficiency. In addition, combination alternatives of AOPs and MBR technologies are also reported for the recycled paper mill effluent.

Table 1
Initial characteristics of the sampled recycled paper mill effluent and the kraft pulp mill effluent used for its experimental treatment trials.

Parameter	Recycled paper mill effluent	Kraft pulp mill effluent
tCOD (mg O_2 L^{-1})	2319 ± 618	1749 ± 435
sCOD (mg O_2 L^{-1})	2031 ± 459	1532 ± 328
BOD_5 (mg O_2 L^{-1})	959 ± 394	850 ± 370
VFA (mg L^{-1})	347 ± 187	285 ± 54
Conductivity (μS cm^{-1})	2322 ± 396	3553 ± 255
Alkalinity (mg $CaCO_3$ L^{-1})	479 ± 184	83 ± 3
TSS (mg L^{-1})	344 ± 261	314 ± 123
Total Nitrogen (mg L^{-1})	11 ± 2	4 ± 1
Phosphorus-PO_4 (mg L^{-1})	1 ± 1	0.88 ± 0.5
Sulphates (mg L^{-1})	496 ± 110	276 ± 38
pH	7.8 ± 0.4	5.0 ± 1.1

2. Materials and methods

2.1. Material and analytical methods

All used chemicals were of analytical grade and supplied by PANREAC S.A. (Barcelona, Spain). The catalyst AEROXIDE® TIO_2 P 25 was supplied by Evonik Degussa GmbH (Essen, Germany). All solutions were prepared in ultrapure water and preserved in the dark.

The final effluents from a recycled paper mill and a kraft pulp mill were sampled and preserved in polyethylene bottles protected from light inside a refrigerator at 4 ± 1 °C until use. Their main analytical characteristics are shown in Table 1. Sample preservation and all analyses were performed according to the standard methods for the examination of water and wastewaters [22].

In particular, chemical oxygen demand (COD), and soluble chemical oxygen demand (sCOD) were measured by the colorimetric method at 600 nm, using an Aquamate spectrophotometer (Thermo Scientific AQA 091801, Waltham, USA) after filtrating the samples through 0.45 μm. pH was adjusted adding 1 M H_2SO_4 or 1 N NaOH when necessary. Colour was estimated using the Pt-Co method, turbidity was determined by the nephelometric method, and volatile fatty acids (VFA) content was measured by the colorimetric method described by Harwood and Huyser [23].

2.2. Experimental procedures

All the following treatments (ozonation, UV or solar TiO_2-photocatalysis, biodegradability test, and MBR) were applied standalone, or in combination (ozonation or solar photocatalysis + biodegradability test, MBR + ozonation or solar photocatalysis) to effluents from the pulp and paper industry taking into account their main characteristics.

2.2.1. Ozonation

Ozonation trials were performed in a glass jacketed cylindrical bubble reactor (height = 1 m, diameter = 5 cm) with a continuous feed of ozone gas (4.0 L min^{-1}) produced from ordinary grade air passed through polycarbonate filters, and subsequently enriched with oxygen. The ozone feeding system consisted of an ozone generator (Model 6020, Rilize, Gijón, Spain), and a flow controller Bronkhorst® (Model F-201AV, Ruurlo, The Netherlands). As a result, 3 g h^{-1} of ozone were continuously fed into the reactor. In order to determine the real ozone consumption inside the reactor, inflow and out-flow ozone concentrations were measured using two on-line ozone analyzers (Model 964C, BMT Messtechnik GMBH,

Berlin, Germany). Therefore, the real specific ozone dose that was consumed in the reactor, which also depends on the nature and concentrations of the compounds being generated along the process, could be measured. Unconsumed ozone was sent to a catalytic ozone destructor.

In addition, a peristaltic pump (Masterflex® Console Drive, Cole-Parmer Instrument Company, IL, USA) was used to recirculate the solution being treated (1.5 L) through the reactor; and probes for pH, redox potential and dissolved oxygen (ProODO, YSI Inc., OH, USA) were used for controlling the process on-line.

Temperature was kept at 25 °C using a thermostatic bath (Model FL300, JULABO Labortechnik GmbH, Seelbach, Germany) that was aided by the reactor's glass jacket itself; and the initial pH of the effluent was set before supplying ozone to the sample. A basic value (pH = 12, supposed to potentially produce better treatment results [24]) and the neutral one (pH = 7, which is closer to the natural values of the effluents; Table 1) were selected to perform this trial. Achieving good results at a lower operational cost avoiding initial pH adjustment would be of valuable application interest. Each ozonation trial was performed for 5 h. Samples were taken every hour for COD, colour, and VFA determination.

2.2.2. Photocatalysis

The photocatalytic process was performed in a reactor with a 450-W high-pressure mercury immersion lamp from ACE-glass (Vineland, USA). The total radiated power in the visible and UV regions was 159.4 W (47.5% and 52.5%, respectively). Major emission bands (>3%) were located at 578.0 nm (12.5%), 546.1 nm (15.4%), 435.8 nm (12.7%), 404.5 nm (6.9%), 366.0 nm (16.1%), 313.0 nm (8.3%), 302.5 nm (4.5%), and 253.7 nm (3.6%). A total photon flux of 1.1×10^{20} photon s^{-1} was calculated, as described in Liang et al. [25], to flow inside the photochemical reactor.

Light intensity was recorded using a radiometer (UV-Elektronik, UV-VIS Radiometer RM-21, Ettlingen, Germany), resulting in 186 mW cm^{-2} between 315 and 400 nm at the mid-height of the UV-lamp, and at 1.5 cm from the light source, which was the actual distance to the sample. The lamp was enclosed inside a quartz glass vessel through which water was circulated to reduce the excessive heat generated during UV irradiation, and it was vertically located in the centre of the reactor. The entire assembly was kept inside a photochemical safety cabinet.

Aeroxide® TiO_2 P25 (Evonik Degussa GmbH, Essen, Germany) was used as the catalyst of the reaction. The main properties of this product are: BET surface area = 50 m^2/g, pore volume = 0.25 m^3/g, and mean particle size of ca. 30 nm. The concentration of TiO_2 and reaction time were optimized at the same two different initial pH values (7 and 12) justified for ozonation, and at a constant temperature of 25 °C. pH, redox potential, and dissolved oxygen were measured on-line during treatment using appropriate probes (ProODO YSI Inc., OH, USA). Each photocatalytic trial was performed for 5 h. Samples were taken every hour for COD, colour, and VFA determination.

2.2.3. Solar photocatalysis

Solar photocatalysis trials were carried out in a solar simulator equipped with a Xenon lamp (300 W) supplied by Newport (Irvine, USA). Intensity and power could be pre-selected for each experimental run, and a filter was used to correct the illuminator out to obtain a solar spectrum under ideal conditions (ASTM E490-73a). The total radiated power in the visible and UV regions was 106.5 W (51.7% and 48.3%, respectively). Major emission bands (>3%) were located at 578.0 nm (17.4%), 546.1 nm (16%), 435.8 nm (10.9%), 404.5 nm (7.5%), 366.0 nm (6.3%), 334.1 nm (4.4%), 313.0 nm (3.9%), 302.5 nm (3.7%), 296.7 nm (3.6%), 289.4 nm (3.2%), and 280.4 nm (3.0%). A total photon flux of 6.8×10^{19} photon s^{-1} was calculated, as described in Liang et al. [25], to flow inside the photochemical reactor.

Light intensity was recorded using a radiometer (UV-Elektronik, UV-VIS Radiometer RM-21, Ettlingen, Germany), resulting in 98.9 mW cm^{-2} between 315 and 400 nm at the mid-surface of the Xe lamp, and at 12 cm from the light source, which was the real distance to the sample.

The concentration of TiO_2 and reaction time were optimized at an initial pH = 7, as it already produced better results in the previously performed photocatalytic trials, and T = 25 °C. pH, redox potential and dissolved oxygen were on-line measured along treatment using adequate probes (ProODO YSI Inc., OH, USA) during the trials.

2.2.4. Biodegradability test

Zahn-Wellens/EMPA Test [26] was used to determine the inherent biodegradability of effluents, for which 7-days-old activated sludge was collected from the wastewater treatment plant located at the recycled paper mill. This biodegradation process was monitored measuring the COD in filtered subsamples subtracted along the reaction until its maximum reduction was achieved.

The functional power of the activated sludge was checked running a parallel test using ethylene glycol as reference substance. Its biodegradability at least reached a 70% COD reduction within the first 14 days of incubation. The ratio of removed COD to its initial value, corrected considering control results, provides the percentage of biodegradation that was achieved along the process.

2.2.5. MBR treatment

The MBR pilot system that was used during combined treatment trials with AOPs was a ZeeWeed-10 from Zenon (GE; Conneticut, USA) with an outside/in ultrafiltration hollow fibre membrane. The membrane module that was used had a mean pore size of 0.04 μm, and an effective filtration area of 0.93 m^2; and the system assembled two process tanks summing up a total effective volume of 70 L. Wastewater was pumped through the membrane by developing a negative pressure (vacuum) across using a gear pump (Verder VGS060.17, maximum 60 L h^{-1}) that was regulated by a frequency controller.

The MBR started up with 70 L of returned activated sludge collected at the wastewater treatment plant installed at the recycled paper mill, and it was fed with effluent from this mill after being subjected to sedimentation. In terms of operation, the process consisted on 300 s of direct filtration, and 20 s of backwash. Solids were removed out via direct filtration.

Sludge drainage was initially set at 0.4 L h^{-1} in order to regulate biomass content inside the MBR, allowing its growth until a target value of solids concentration was reached. Subsequently, values between 0.4 and 0.9 L h^{-1} were set to regulate the concentration of solids inside the tanks. The biomass inside the MBR was controlled measuring mixed liquor volatile suspended solids (MLVSS), which average value resulted 5.92 g L^{-1}. Average sludge age was 16 days at 24 h of hydraulic retention time (HRT), and 5 days at 8 h HRT. Total suspended solids (TSS), turbidity, COD, VFA, MLSS (mixed liquor suspended solids), MLVSS, total nitrogen, and phosphate contents were measured twice a week during the trials.

3. Results and discussion

3.1. Comparative assessment of the advanced oxidation treatment of effluents from pulp and paper industry

3.1.1. Ozone treatment

The required ozone dose for an optimal treatment and the efficiency of the process therefore, were dependent on the concentration of ozone in the inlet gas, reaction time [27], and the

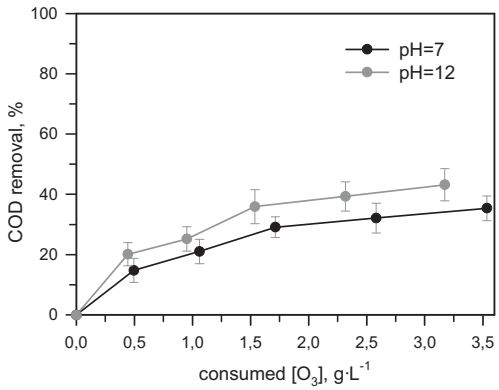

Fig. 1. COD reduction obtained along the treatment of the effluent from a recycled paper mill by ozonation.

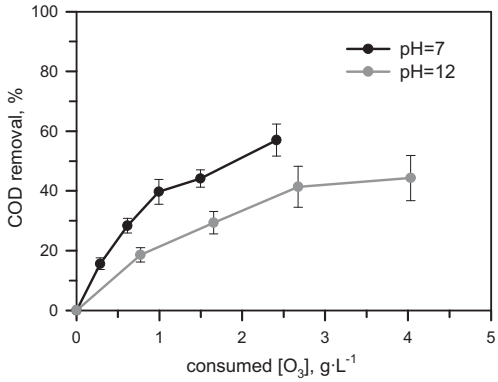

Fig. 2. COD removal obtained along the treatment of the effluent sampled at a kraft pulp mill by ozonation.

nature and concentrations of organic and inorganic compounds in the treated effluent. In short, the evolution of ozone consumption resulted different during treatment (Figs. 1 and 2) because of the continuous reaction of ozone with the changing content of organic and inorganic compounds present in the solution. As a result, the real specific ozone dose that was consumed in the reactor reached 3.6 mg O_3 per mg of removed COD for the effluent from the recycled paper mill, and 2.38 mg O_3 per mg of removed COD for the effluent from the kraft pulp mill, when 2.4 g L^{-1} of ozone were consumed at an initial pH = 7; as it can be calculated from Figs. 1 and 2.

In fact, the ozone treatment of the effluent from the recycled paper mill showed a lower reduction of the COD (Figs. 1 and 2), which may be attributed to its higher concentration of compounds that are difficult to oxidize (VFA, mainly); and a higher amount of bicarbonate (Table 1), which has been previously reported to produce certain scavenging effect [28]. In short, aliphatic organic compounds have previously widely been described to be difficult to oxidize by AOPs [29,30], resulting in an increase of the specific consumption of ozone, and the consequent decrease of the efficiency of the treatment. As a result, about a 60% reduction of the COD was achieved ozonating the effluent of the kraft pulp mill at an initial pH = 7 (2.4 g L^{-1} of consumed ozone; Fig. 2); whereas this treatment only reached about a 35% COD removal for the effluent of the recycled paper mill (Fig. 1).

Although several authors have reported a higher effectiveness of ozone treatment at basic pH values [1,5,24], because the formation of hydroxyl radicals is expected to be more efficient [3,31], the ozonation of the recycled paper mill effluent only showed some non-significant differences ($p < 0.05$) between the achieved COD removals at an initial pH = 7 and pH = 12 (Fig. 1). On the other hand, the application of this treatment to the effluent from the kraft pulp mill resulted in a significant higher COD reduction at an initial pH = 7 than at pH = 12 (Fig. 2). These results may be the consequence of the usual high alkalinity figures that characterize effluents from pulp and paper mills (Table 1), which might have scavenged hydroxyl radicals at high pH values; whereas it may otherwise be rather beneficial at a lower pH value buffering the process [28].

In addition, a higher ozone dose than the strictly being devoted to oxidation might have been required at pH = 12 because higher pH values may also accelerate the decomposition of ozone; so its specific overall consumption per unit of removed COD was therefore higher than the expected to just perform the oxidation treatment [28]. In conclusion, whatever particular side effects were affecting the process, results showed that these effluents would be suitable for their (almost) best oxidation treatment at their usual neutral pH value; therefore avoiding the cost of pH control operations at industrial scale.

The ozone treatment of these effluents was performed through consecutive oxidation stages (Figs. 1 and 2) involving different ozone dosage consumptions depending on the organic load of the solution, and the initial pH value of the effluent. In short, two main reaction stages do really consecutively happen along the process: (1) a first one where easily oxidizable compounds were mainly degraded; and (2) a second one where oxi-recalcitrant by-products (VFA mainly [32,33]) that are formed along the process are attempted to be further oxidized [2,12]. As a result, a steepest removal of the COD was shown at the beginning of the process due to the effective degradation of oxidable products (0.5–1.0 g L^{-1} O_3, depending on the type of effluent; Figs. 1 and 2); whereas reaction efficiency thereafter turned to progress smoothly as the content of oxi-recalcitrant by-products increased in the solution even though ozone dosage progressively rose as well. In fact, the limitation of TOC abatement is one of the results of this increasing accumulation of oxi-recalcitrant compounds [34]; although they are generally characterized for being highly biodegradable, which enables the possibility of adding a biological treatment stage afterwards.

3.1.2. Photocatalysis

The maximum reduction of the COD that was achieved treating the same pulp and paper effluents by photocatalysis resulted lower than the figures just reported for their ozonation (Figs. 1 and 2) in all the tested cases, whether using UV light (≈20–25%; Fig. 3), or assisting the process with a solar simulator (≈25–30%; Fig. 4); just as it would have been expected from previously reported trials [1,2,35].

Although degradation results showed the same tendency whichever light source was used, the reduction of the COD resulted slightly higher (<5%) when the solar simulator was used, particularly at the higher tested TiO_2 concentration level (10 g TiO_2 L^{-1}; Figs. 3 and 4). This particular might ultimately be explained in terms of differential characteristics of the incident light, and other properties of the used reactors that might have somehow changed the distribution and efficiency of the suspended catalyst. In this case, using the sun as light source would at least result in the reduction of the energetic cost of the treatment without meaning any efficiency loss.

In addition, similar non-significant slight COD removal differences were also found between the photocatalytic treatments of both tested effluents, resulting that higher treatment efficiency was

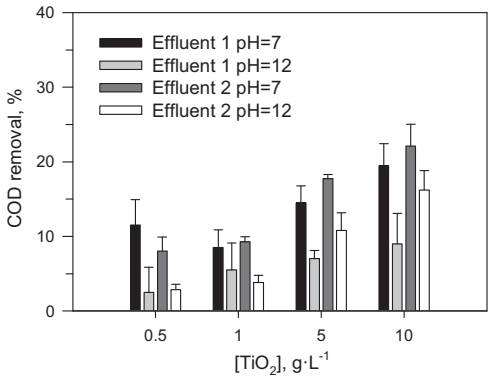

Fig. 3. COD reduction achieved in the UV-photocatalytic treatment of effluents from a recycled paper mill (effluent 1) and a kraft pulp mill (effluent 2).

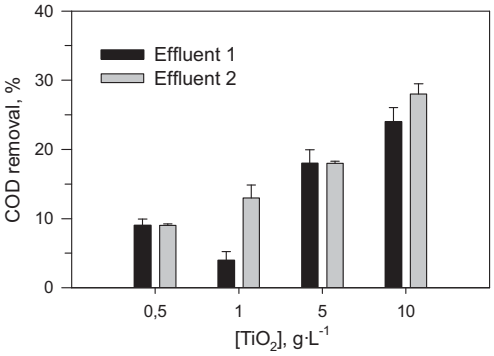

Fig. 4. COD removal results for the solar photocatalytic treatment performed at an initial pH = 7 of effluents from a recycled paper mill (effluent 1) and a kraft pulp mill (effluent 2).

achieved for the effluent from the kraft pulp mill; as it has also been reported for its ozone treatment, and may also be partially explained by the higher content of oxi-recalcitrant aliphatic organic compounds that is present in the effluent sampled at the paper mill (e.g. VFA content in Table 1).

The efficiency of these photocatalytic processes was much influenced by the dosage of TiO_2 (Figs. 3 and 4), resulting in a higher degradation of organics when the TiO_2 concentration was also higher (up to 10 g TiO_2 L^{-1}) regardless the light source (UV or solar) and initial pH value (7 or 12) that were used. These results are in accordance with those reported in Chang et al. [16] for a similar treatment of lignin powder. A concentration of TiO_2 higher than 10 g L^{-1} was not considered in the trials because it has previously been reported to cause a shadow effect interfering with the transmission of light, so the generation of electron–hole pairs cannot effectively occur under such excessive catalyst content [15,16].

Although several authors have reported good reductions of organic compounds performing photocatalytic treatment at both neutral and basic initial pH values [15,16,36], the fact is that removal of the COD resulted higher when UV-photocatalysis was performed at pH = 7 for both types of effluents (Fig. 3). This may partially have been caused by the more or less strong competition that anions, cations, and some neutral molecules exert against organic contaminants for the reactive sites on the surface of TiO_2 particles; thus decreasing the overall process efficiency whether being performed at basic or acid pH values. In short, the reaction rate

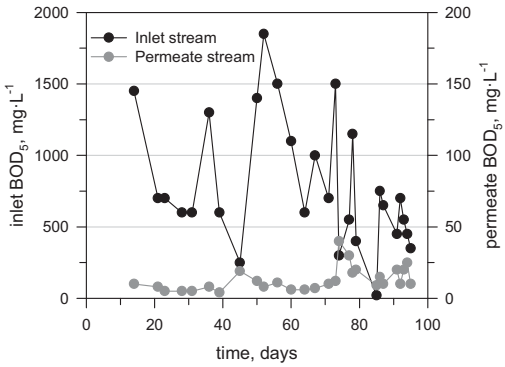

Fig. 5. COD and BOD_5 concentration contents during the start-up piloting of the MBR.

would have been slowed down by anion adsorption on the surface of the positively charged catalyst under acid conditions; whereas catalytic particles negatively charge, and the presence of cations might therefore have moderated the reaction rate, under basic pH values [37].

3.2. The combination of AOPs and biological treatment to an effluent from a recycled paper mill

3.2.1. MBR start-up

There were initially 4 g L^{-1} of volatile suspended solids in the MBR, which were increased to average 5–6 g L^{-1} along the biological treatment performance. A higher concentration of 8 g L^{-1} was also tested, but treatment efficiency was not significantly enhanced, and an excessive membrane fouling was generated. Total suspended solids averaged about 2 g L^{-1} higher values than the content of volatile suspended solids.

The COD values measured in the permeate flowing out the MBR were very stable during all the process despite the variability of inlet wastewater quality (Fig. 5). The average sCOD value of this permeate was 250 mg O_2 L^{-1} when HRT was kept for 24 h [feed/microorganisms (F/M) ≈ 0.44 kg COD/kg MLSS day], and 500 mg O_2 L^{-1} when HRT was also evaluated at 8 h [(F/M) ≈ 1.21 kg COD/kg MLSS day], which is close to the actual value that is used in this and other similar mills.

Sludge age resulted 16 days, and sludge retention time (SRT) was about 7.3 days for a 24 h HRT. This short SRT favoured the enrichment of the sludge with bacterial species of high growth rate [38]. Particularly, a similar short SRT has also previously been reported addressing that the COD of the effluent was not influenced by changing SRT [38,39]. In addition, it is also well-known that a longer SRT favours the growth of specialized bacteria enhancing the breakdown of large macromolecules [40], the sludge of the MBR was previously acclimated to the wastewater to be treated in this particular case, and a longer SRT was not therefore finally required for an efficient biological treatment. In fact, the MBR effectively worked removing all biodegradable COD; therefore producing an appropriate effluent to be tested for an oxidation post-treatment.

BOD_5 values of permeate were often lower than 10 mg O_2 L^{-1} during the first stage of HRT = 24 h; and they resulted even slightly higher for HRT = 8 h. A total to an almost complete degradation of biodegradable organic matter was finally achieved by this treatment (Fig. 5). In addition, turbidity was in average reduced from 300 to 2 NTU; whereas suspended solids were totally removed.

The membrane always showed a good behaviour during treatment; although the optimization of this membrane treatment is

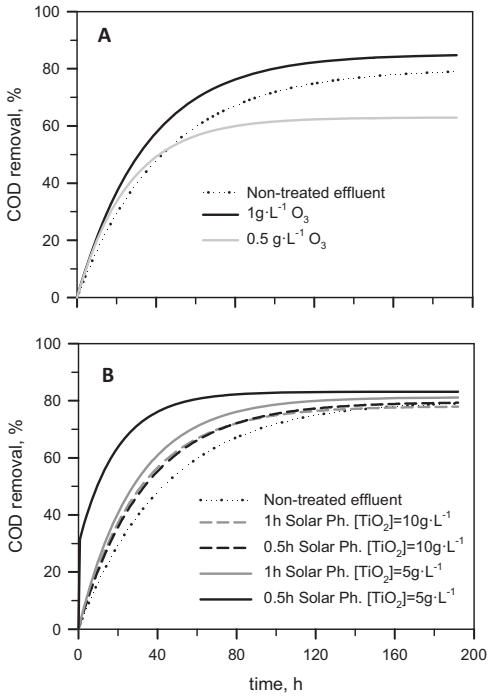

Fig. 6. Zhan Wallens biodegradability test applied to the effluent from the recycled paper mill whether having previously been oxidized by ozone (A), solar photocatalysis (B), or not.

not herewith reported because it would not result representative for industrial application. In fact, it would be necessary to perform pilot trials with membrane systems of similar characteristics than those that will be applied at industrial scale, which generally use a small number of full-scale membranes modules, in order to obtain scalable results of this type of MBR system [41].

3.2.2. The combination of AOPs with biological post-oxidation treatment

In short, the oxidation treatment of the effluent from a recycled paper mill showed worse results than the effluent from the kraft pulp mill; but biodegradability results were much higher (≈75%). Therefore, the combination of AOPs with a biological post-treatment was also tested in order to assess whether COD reduction efficiency might be improved for the effluent from the recycled paper mill, considering the expected capacity of AOPs to increase the biodegradability of this type of effluents [3,5,13], and that it would imply a lower overall treatment cost. Solar radiation was the only photocatalytic treatment being assessed because it showed similar to even better results than UV-light, and its application would also be much cheaper.

A balance between the potential cost of treatment alternatives and their efficiency was considered when selecting the reaction conditions of each AOP + biological combination treatment. Considering the above reported results for standalone AOPs, the following best treatment conditions were tested: (a) 1 and 0.5 g L^{-1} of ozone at pH = 7 for ozonation; and (b) 5 and 10 g L^{-1} of TiO_2 along 0.5 and 1.0 h of solar photocatalytic treatment at pH = 7 as well. In addition, the effluent's threshold of biodegradability was determined before performing oxidation in order to properly compare it with the biodegradability results of the already oxidized effluent (Fig. 6).

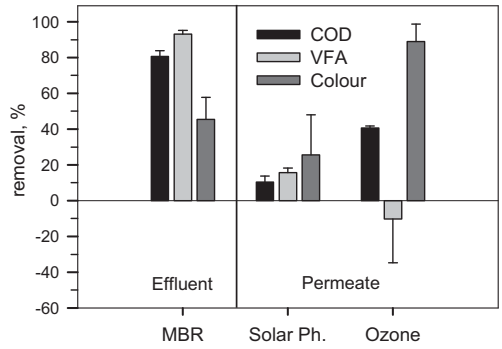

Fig. 7. Degradation efficiency results of the MBR biological treatment of the effluent from a recycled paper mill, and the oxidation post-treatment of its permeate by solar photocatalysis and ozonation.

In summary, COD reduction did not result strongly improved after any previous oxidation process; although 1 g L^{-1} ozone treatment and 5 g TiO_2 L^{-1} photocatalytic process slightly enhanced biodegradability (≈5%; Fig. 6). On the other hand, 10 g TiO_2 L^{-1} solar photocatalysis did not particularly result in higher post-biological COD reduction probably because a greater amount of biodegradable organic matter was already consumed during the oxidative process, as addressed by the better efficiency figures that were achieved when this treatment was performed standalone (Fig. 4).

3.2.3. The application of AOPs as post-MBR biological treatment

Finally, the effluent from the recycled paper mill was firstly treated in the MBR, and the generated permeate was thereafter treated by ozonation and solar photocatalysis in order to assess the overall efficiency of this treatment strategy as well. Those reaction conditions addressing better biodegradability results (Fig. 6) were also applied in these trials, that is: (a) 1 g O_3 L^{-1} for ozonation, and (b) 5 g TiO_2 L^{-1} for a 30 min solar photocatalysis; both performed at pH = 7.

The standalone MBR treatment reached an 80% COD reduction with an almost total consumption of organic fatty acids (VFA), and a reduction of colour higher than the 40% (Fig. 7). The 20% remaining COD in its permeate was mainly made up of bio-recalcitrant COD, thus susceptible of being further treated by AOPs. In fact, the ozone oxidation of this permeate achieved a further 40% reduction of the remaining COD (Fig. 7); thus enhancing the overall COD removal a significant additional 10% approx. (Fig. 8). On the other hand, solar photocatalysis only achieved an extra 10% removal of the COD outlasting biological treatment (Fig. 7). In addition, ozone was able to almost completely remove persisting colour in the permeate (≈95%); as well as it produced an increase of VFA content, thus enabling the recirculation of the ozonized permeate back to the MBR in order to further increase treatment efficiency.

In summary, although all tested configurations combining biological and advanced oxidation processes resulted in the enhancement of the overall reduction of the COD, the highest COD removal was achieved treating the effluent from the recycled paper mill by a biological stage followed by the ozone treatment of the generated permeate (Fig. 8). In short, the remaining bio-recalcitrant fraction could be more efficiently ozonized when the initial biodegradable load of this effluent was previously biologically removed. Nevertheless, the biological process was able to efficiently remove most of its contaminant load; so ozone post-treatment would only be required when very stringent discharge requirements, in both quantity and/or quality terms, may be imposed.

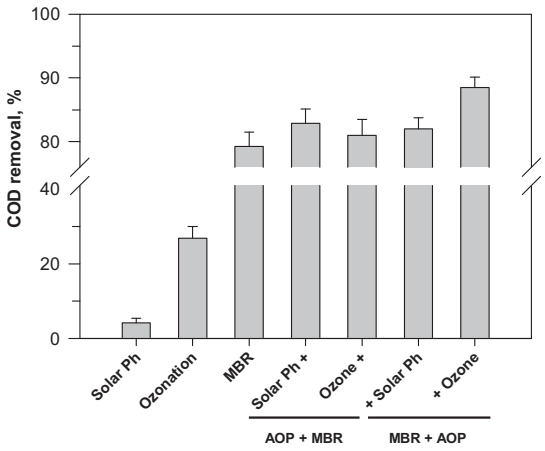

Fig. 8. Comparison of solar photocatalysis and ozonation as pre- and post-treatment alternatives of the MBR biological treatment of the effluent of a recycled paper mill.

4. Conclusions

The treatment of effluents from pulp and paper mills was highly influenced by the composition of each type of wastewater, resulting that effluents from recycled paper mills were more biodegradable than those generated in kraft pulp mills. In consequence, better results were obtained when the kraft pulp mill effluent was treated by AOPs.

Ozonation achieved a higher COD reduction than photocatalysis, that was about a 35% for the effluent from a recycled paper mill, and about a 60% for the effluent sampled at a kraft pulp mill at an initial pH = 7.

Photocatalysis achieved lower COD removals treating both effluents under the best designed reaction conditions; namely, about a 25% for the effluent from the recycled paper mill and almost the 30% for the effluent from the kraft pulp mill.

The effluent from the recycled paper mill was successfully treated in a membrane bioreactor thanks to its high biodegradable nature; thus achieving a very high reduction of the COD (80%).

The combination an AOP pre-treatment with an MBR biological process did not result in a significant higher overall efficiency.

In addition, the combination of an MBR biological stage with a TiO_2-photocatalysis post-treatment only reported a slight improvement of a further 10% reduction of the COD.

On the other hand, the combination of this biological process with an ozonation post-treatment achieved very good removals of COD and colour (approx. 90% and 95%, respectively); as well as it increased the biodegradability of the final effluent, therefore allowing the potential successful recirculation of the resultant wastewater back to receive further MBR treatment.

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PAPER III

D. Hermosilla, **N. Merayo**, R. Ordóñez, A. Blanco

Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill

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Optimization of conventional Fenton and ultraviolet-assisted oxidation processes for the treatment of reverse osmosis retentate from a paper mill

Daphne Hermosilla *, Noemí Merayo, Ruth Ordóñez, Ángeles Blanco

Department of Chemical Engineering, Complutense University of Madrid, Facultad de Ciencias Químicas, Ciudad Universitaria s/n, 28040 Madrid, Spain

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ABSTRACT

According to current environmental legislation concerned with water scarcity, paper industry is being forced to adopt a zero liquid effluent policy. In consequence, reverse osmosis (RO) systems are being assessed as the final step of effluent treatment trains aiming to recover final wastewater and reuse it as process water. One of the most important drawbacks of these treatments is the production of a retentated stream, which is usually highly loaded with biorecalcitrant organic matter and inorganics; and this effluent must meet current legislation stringent constraints before being ultimately disposed. The treatment of biorefractory RO retentate from a paper mill by several promising advanced oxidation processes (AOPs) – conventional Fenton, photo-Fenton and photocatalysis – was optimized considering the effect and interaction of reaction parameters; particularly using response surface methodology (RSM) when appropriate (Fenton processes). The economical cost of these treatments was also comparatively assessed. Photo-Fenton process was able to totally remove the COD of the retentate, and resulted even operatively cheaper at high COD removal levels than conventional Fenton, which achieved an 80% reduction of the COD at best. In addition, although these optimal results were produced at pH = 2.8, it was also tested that Fenton processes are able to achieve good COD reduction efficiencies (>60%) without adjusting the initial pH value, provided the natural pH of this wastewater was close to neutral. Finally, although TiO_2-photocatalysis showed the least efficient and most expensive figures, it improved the biodegradability of the retentate, so its combination with a final biological step almost achieved the total removal of the COD.

1. Introduction

Reducing water use is considered among current most important environmental issues in pulp and paper industries (Ordoñez et al., 2009), which are adopting zero liquid effluent policies, including the closure of water circuits (Koppol et al., 2004), to minimize the use of fresh water. As a result of implementing such management policies, the water consumption within the paper sector has decreased much worldwide. In fact, the generation of wastewater has been significantly reduced from 46 m^3/t of paper in 1974 (Mobius and Helble, 2004) to around current 15 m^3/t (Sundholm, 2000). Examples of actual current fresh water consumption figures in some paper mills are: 0–4 m^3/t of packaging paper, and 8–16 m^3/t of newsprint, printing paper, tissue paper, or market pulp (BREF, 2011).

As high water quality is required for replacing fresh water use in some stages of the paper mill, like high pressure showers, reverse osmosis (RO) systems are being implemented as the final step of different treatment trains aiming to recover the final effluent from the mill and reuse it as process water. Although RO filtration ensures an almost total conductivity reduction and the removal of all pathogens (Asano and Cotruvo, 2004), its wider application is still limited by technical and financial challenges related to the disposal of the retentate (Greenlee et al., 2010a). Even though much research effort has been successfully devoted to reduce the generated retentate increasing the recovery efficiency of RO systems (e.g. Greenlee et al., 2010a,b; Ning and Troyer, 2009), this trend inevitably results in a progressive higher concentration of pollutants in the retentated fraction, making more difficult meeting effluent discharge thresholds without performing a properly designed wastewater treatment previously.

Provided biological treatments are not able to remove biorecalcitrant compounds, which are usually present in this type of industrial effluent at high concentration levels (Ordoñez et al., 2010), new alternative technologies are called to integrate current treatment trains. Particularly, advanced oxidation processes (AOPs) have been shown able to successfully remove such biorecalcitrant substances. Achieving a partial oxidation of non biodegradable organics (e.g. lignin and chlorinated structures) increases wastewater biodegradability enough to perform further successful biological treatment (Amat et al., 2005).

* Corresponding author. Tel.: +34 91 394 4645; fax: +34 91 394 4243.
E-mail address: dhermosilla@quim.ucm.es (D. Hermosilla).

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Fenton process is one of the most common AOPs used for wastewater treatment because it is usually very efficient and implies a lower economical cost than others (e.g. Esplugas et al., 2002). Regardless a high COD removal efficiency could be achieved and its relative environmental friendliness, the Fenton treatment of wastewater is limited by the final production of iron sludge, which requires ultimate disposal (Pignatello et al., 2006). In order to minimize the generation of iron sludge adding just a catalytic ferrous iron content that is photo-recovered (Hermosilla et al., 2009b), the conventional Fenton process may be positively assisted by the application of UV-light, which furthermore enables the treatment of carboxylates by photo-decarboxylation (Hermosilla et al., 2009a).

On the other hand, recent research progress has been addressed on the application of reusable catalysts in UV-assisted AOPs, such as photocatalytic processes performed with titanium dioxide (TiO_2) (e.g. Chong et al., 2010). Particularly, heterogeneous photocatalysis catalyzed by TiO_2 has been shown to efficiently remove color and dissolved organic carbon (DOC) from ECF bleaching effluents and other solutions containing lignin. In addition, a rapid decrease of toxicity has been also reported for different solutions (Catalkaya and Kargi, 2007; Chang et al., 2004); as well as biodegradability may be enhanced enough to consider these photocatalytic processes as interesting pre-oxidation steps preceding biological treatment (Oller et al., 2011).

In short, the potential application of optimized conventional Fenton and photo-assisted oxidation processes, whether using Fe^{2+} or TiO_2 as catalyst, as novel promising alternatives for the treatment of the biorecalcitrant organic fraction present in RO retentate from a recovered paper mill is going to be assessed next.

2. Material and methods

2.1. Material and analytical methods

RO retentate was sampled from the last treatment step of a pilot plant placed inside a newsprint paper mill located in Madrid (Spain) that uses 100% recovered paper as raw material. This pilot trial was performed aiming to assess the feasibility of reclaiming the current paper mill effluent and reuse it within the process. The pilot plant combined biological (anaerobic + aerobic) and membrane filtration (UF + RO) technologies to treat wastewater flowing out from a dissolved air flotation unit placed in the first water loop of the deinking plant, which is the most contaminated stream of the paper mill.

The sampled RO retentate, which main analytical characteristics are shown in Table 1, was preserved in polyethylene bottles protected from light inside a refrigerator at 4 ± 1 °C. Mid-strength biorefractory organic and inorganic loads characterized the sample (Table 1), as expected for this type of waste stream (Ordoñez et al., 2010). Sample preservation, all analyses, and measurements described next were performed according to the standard methods for the examination of water and wastewaters (APHA, AWWA and WPCF, 2005). All used chemicals were of analytical grade and were supplied by PANREAC S.A. (Barcelona, Spain).

Chemical oxygen demand (COD) was measured by the colorimetric method at 600 nm using an Aquamate spectrophotometer (Thermo Scientific AQA 091801, Waltham, USA). A TOC analyzer (Apollo 9000, Tekmar Dohrmann, Ohio, USA) was used to measure total organic carbon (TOC) by the combustion infrared method. H_2O_2 concentration was determined using the titanium sulfate spectrophotometric method (Pobiner, 1961). Fe^{2+} concentration was determined using the 1,10-phenanthroline colorimetric method (Tamura et al., 1974); using ammonium fluoride as masking agent for ferric iron (Fe^{3+}) to avoid its potential interference in the measure. Total soluble iron concentration was measured reducing Fe^{3+} to Fe^{2+} iron adding hydroxylamine under acidified conditions, and then determining Fe^{2+} concentration as just described. pH was adjusted adding 1 M H_2SO_4 or 1 N NaOH when required.

Table 1
Chemical characterization of the treated RO retentate from a paper mill.

Parameter	Units	Average	Standard deviation
Temperature	°C	23	2
pH		7.5	0.5
CODt	mg/L	530	74
TOC	mg/L	111	13
BOD_5	mg/L	21	4
TSS	mg/L	21	7
Conductivity	μS/cm	3679	564
Alkalinity	mg $CaCO_3$/L	750	0
P-total	mg/L	12	5
N-total	mg/L	105	22
NH_4^+–N	mg/L	17	1
NO_3^-	mg/L	45	16
Cl^-	mg/L	197	30
SO_4^{2-}	mg/L	460	19
SiO_2	mg/L	190	11
F^-	mg/L	0.28	0.11
B	mg/L	0.86	0.03
Al	mg/L	0.06	0.00
K	mg/L	18	0.60
Na	mg/L	871	97
Mg	mg/L	8	0.55
Ca	mg/L	97	7
Fe^{2+}	mg/L	1.86	1.18
Fe-total	mg/L	1.87	0.08

2.2. Experimental procedures

2.2.1. Fenton process

The total solution volume in the reactor was 2 L. The sample to be treated was mixed inside using a magnetic device, and the temperature was adjusted to the desired value with a water heating and circulating device. The following operational reaction parameters were optimized following the methodology described next in the experimental design section: pH, reagent concentrations and reaction time. Considering that it has been reported that a change in temperature from 25 to 45 °C does not significantly affect the removal of COD in the Fenton treatment of other wastewater (Hermosilla et al., 2009b; Kang and Hwang, 2000; Rivas et al., 2005; Zhang et al., 2005), reaction temperature was set at 25 °C to avoid an unnecessary consumption of heating energy, provided this value is approximately the natural temperature at which RO retentate was sampled (Table 1).

Ferrous sulfate ($FeSO_4$) was added to reach the targeted Fe^{2+} concentration after the initial pH value was adjusted, which was thereafter monitored but not further controlled along the treatment. H_2O_2 was then added in batch mode until the desired concentration was reached. Fe^{2+} and total iron concentration, total COD, soluble COD, and soluble TOC were measured just before the addition of H_2O_2, which was considered as reaction time = 0. Aliquots of treated solution were periodically sampled with a syringe thereafter. These samples were neutralized to pH ≈9.00 adding 40% sodium hydroxide (NaOH), and then centrifuged during 15 min at 2000 rpm. COD, TOC, H_2O_2 concentration, and turbidity were measured in the collected supernatant. H_2O_2 concentration values were used to correct COD values according to Hermosilla et al. (2009b). Treatments were run until H_2O_2 was totally consumed, so maximum COD removal was surely achieved for a set of reaction variables values.

2.2.2. Photo-Fenton process

The UV-assisted Fenton treatment of the sampled RO retentate was optimized following the same experimental procedure just

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describe above, plus a 450 W high-pressure mercury immersion lamp (ACE-glass, Model 7825-34, Vineland, USA) assisted the Fenton process. This lamp was located vertically in the center of the reactor enclosed inside a quartz glass vessel through which water was circulated to reduce excessive heat generated during irradiation. In addition, cooling water flowing through the double-walled immersion well eliminated the infrared spectrum of the light. The entire assembly was kept inside a photochemical safety cabinet (ACE-glass, Vineland, USA). The total power radiated in the visible and UV regions was 159.4 W (47.5 and 52.5%, respectively). Major emission bands (>3%) were located at 578.0 nm (12.5%); 546.1 nm (15.4%); 435.8 nm (12.7%); 404.5 nm (6.9%); 366.0 nm (16.1%); 313.0 nm (8.3%); 302.5 nm (4.5%); 253.7 nm (3.6%). A total photon flux in the photochemical reactor of $1.1 \cdot 10^{20}$ photons/s was calculated as described in Liang et al. (2011). Light intensity was recorded using a radiometer (UV-Elektronik, UV–VIS Radiometer RM-21, Ettlingen, Germany), resulting in 186 mW/cm^2 between 315 and 400 nm, at the mid-height of the UV-lamp, and 1.5 cm from the light source, which was the distance between sample and irradiation source. The UV-lamp was switched on just before H_2O_2 was added (reaction time = 0).

2.2.3. Photocatalysis

Photocatalytic treatment was performed using a similar experimental procedure and the same UV-lamp equipment just described for the photo-Fenton process despite no H_2O_2 was added to promote HO• generation, and TiO_2 (AEROXIDE® TIO_2 P 25, Evonik Degussa GmbH, Essen, Germany; BET surface area = 50 m^2/g; pore volume = 0.25 m^3/g, and mean particle size of ca. 30 nm) was used as reaction catalyst instead Fe^{2+}. Although several semiconductor catalysts have been proved to increase the treatment efficiency of UV light, TiO_2 has received much greater attention in photocatalysis technology research and development initiatives (Chong et al., 2010); and it has been particularly reported that TiO_2 is more efficient than ZnO, whether immobilized on glass or not (Yeber et al., 1999, 2000). Considering that photocatalytic processes performed with suspended catalysts have furthermore resulted as efficient as when they are supported, which might even require a longer reaction time (Chong et al., 2010; Yeber et al., 1999, 2000), it was finally designed to perform the treatment with suspended TiO_2. The concentration of TiO_2 and reaction time were optimized keeping a constant pH (as received, pH = 7.5) and temperature (T = 25 °C). These values of pH and temperature have been reported to produce optimum results previously (Chang et al., 2004; Merayo et al., 2010), and they imply significant savings on reagents consumption and heating energy. The suspension was first stirred in the dark for 10 min before irradiation (reaction time = 0). This was sufficient to reach an equilibrated adsorption as deduced from the steady state concentrations. Subsequently the UV-lamp was switched on.

Considering that this photocatalytic process may be an interesting pre-oxidation step preceding biological treatment (Yeber et al., 2000), Zahn-Wellens/EMPA Test (US EPA 712-C-98-084, 1998) was used to determine the inherent biodegradability of the resulting solution after performing TiO_2-photocatalytic treatment to the sampled RO retentate. In short, a mixture containing the test substance, mineral nutrients and activated sludge in aqueous medium is shook and aerated at 20–25 °C under diffuse light for up to 28 days of incubation. Seven-days-old activated sludge was collected from the wastewater treatment plant located in the mill. Blank controls containing activated sludge and mineral nutrients but no test substance were run in parallel. This biodegradation process was monitored measuring COD in filtered subsamples until the maximum reduction of the COD was achieved. The functional power of the activated sludge was checked running a parallel test using ethylene glycol as a reference substance, which biodegradability achieved at least a 70% COD removal within 14 days of incubation. The ratio of the removed COD, corrected considering control results, to the initial COD value provides the percentage of biodegradation over time.

2.3. Experimental design

Response surface methodology (RSM) was used to assess the influence of the considered reaction variables as well as its interactive effect (Mason et al., 2003; Torrades et al., 2011; Wu et al., 2010) in order to optimize the Fenton and photo-Fenton treatments of RO retentate. RSM allows determining the optimal operation conditions for the reaction whether at least enclose the range of values satisfying operating specifications (Dopar et al., 2010; Wu et al., 2010; Zhu et al., 2011). Experimental design, regressions and response surfaces were calculated by SYSTAT 13 (SYSTAT Software Inc., Chicago, USA). As TiO_2 concentration and reaction time were the only two variables considered in the photocatalytic treatment, there was no need to run RSM to optimize the process.

Provided reaction time is dependent of the concentration of reagents, this variable was optimized leaving enough time to achieve asymptotical treatment efficiency in terms of removal of the COD (Hermosilla et al., 2009b; Zhang et al., 2005). As a reference, the theoretical stoichiometrical relation between the COD and the required H_2O_2 quantity to generate enough HO• to totally oxidize the organic matter is 2.125 (Kim et al., 1997), although a higher optimum value is expected due to parallel reactions and inefficiencies of the process (Hermosilla et al., 2009b; Pignatello et al., 2006). In addition, recent research has well stated that a $[H_2O_2]/[Fe^{2+}]$ molar ratio of 1.5, which also considers process efficiency losses, and a pH value of 2.8, produce optimum results for the Fenton treatment of other highly concentrated streams (Hermosilla et al., 2009b; Zhang et al., 2005). Therefore, RSM was performed considering H_2O_2 concentration levels of 1.0625, 2.125 and 4.250x initial COD value (mg/L); $[H_2O_2]/[Fe^{2+}]$ molar ratios of 1.0, 1.5 and 2.0 for the Fenton treatment, and up to 30 for the photo-Fenton treatment. $[Fe^{2+}]$ present in the effluent (Table 1) was considered in the calculations. Hermosilla et al. (2009b) reported up to a 32 times lower use of $FeSO_4$ thanks to the photo-regeneration of Fe^{2+} from Fe^{3+}); and pH values of 2.8, 5.0 and 7.2. It is of particular interest assessing whether shifting to closer values to the natural pH value of the treated stream (7.5 ± 0.5; Table 1) may not suppose great treatment efficiency losses. All experiments were repeated three times.

RSM regression analysis was performed according to a full factorial design (N = 27) using the following quadratic model:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} X_i X_j$$

where Y (COD removal) is the process response dependent variable, X_i are the considered independent variables (X_1 = $[H_2O_2]$/COD; X_2 = $[H_2O_2]/[Fe^{2+}]$: X_3 = pH); and b_i, b_{ii} and b_{ij} are the corresponding regression coefficients.

3. Results and discussion

The application of RSM multiple regression analysis to Fenton process results produced the following quadratic model: COD = 59.244 + 17.935·X_1 + 22.189·X_2 − 8.052·X_3 − 1.969·X_1^2 − 6.721·X_{2}^{2} + 0.556·X_3^2 − 0.191·X_1·X_2 − 0.519·X_1·X_3 − 0.549·X_2·X_3. This model resulted highly significant (F = 20.44; p < 0.001), and the prediction accuracy of the model in terms of the multiple R of the regression was 0.957. The corresponding model generated for the results of the performed photo-Fenton trials was: COD = 60.215 + 34.775·X_1 + 0.555·X_2 − 8.210·X_3 − 4.610·X_1^2 + 0.024·X_2^2 +

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$0.539 \cdot X_3^2 + 0.039 \cdot X_1 \cdot X_2 - 1.100 \cdot X_1 \cdot X_3 - 0.351 \cdot X_2 \cdot X_3$. Prediction accuracy and significance of this model were also very high (multiple R of the regression = 0.974, $F = 35.07$, $p < 0.001$).

3.1. Conventional Fenton treatment

3.1.1. Assessing the effect of pH

pH has been addressed as one of the main factors limiting the performance of the Fenton treatment of wastewater, playing a major role in the control of the activity of the oxidant and the substrate, the stability of H_2O_2 itself, and the speciation of iron (Gulsen and Turan, 2004; Hermosilla et al., 2009b; Zhang et al., 2005). As pH increases, iron precipitates as $Fe(OH)_3$ (Kiwi et al., 1993), and H_2O_2 is decomposed to oxygen (Pulgarin and Kiwi, 1996). On the other hand, when pH is less than 4, inorganic carbon can be also removed, limiting its HO• scavenging activity (Buxton et al., 1988), and the solubility of iron increases (Kiwi et al., 1993), improving the overall efficiency of the process. In addition, a continuous pH control operation along the treatment usually implies a higher economical cost and causes the conductivity of the solution to rise. Therefore, the limit for effluent conductivity set by current environmental legislation may limit its disposal.

The designed RSM identified pH = 2.8 as the optimal value for the Fenton treatment of the sampled RO retentate from the paper mill (Fig. 1), which has been also reported optimal previously for the performance of this treatment to landfill leachate (Hermosilla et al., 2009b) and phenol (Kavitha and Palanivelu, 2004). In addition, it is important to consider the possibility of implementing this process at natural effluent pH values, which is close to neutral (pH ≈7.5, Table 1); therefore avoiding an extra cost for controlling the pH, and potential trouble that may be caused by an increased effluent conductivity. In fact, reasonable reductions of the COD (60–70%) were achieved working from an initial pH = 7.2, but at higher reagents dosage (Fig. 1).

pH decreased naturally to 2.8 along the reaction when the initial value in the solution was higher, up to neutral (Fig. 2), an effect that has been previously attributed to the production of CO_2 and fatty organic acids as other organic compounds are oxidized (Hermosilla et al., 2009a). This way, the influence of an initial higher pH value than the optimum is partially compensated by an increase in the consumption of H_2O_2; but certain oxidation efficiency loss is always addressed due to the decomposition of the oxidants, a lower solubility of iron, and parallel reactions (Gulsen and Turan, 2004; Pulgarin and Kiwi, 1996; Zhang et al., 2005).

3.1.2. Optimizing the required quantity of reagents

The use of chemical reagents is a major operational cost item when implementing Fenton treatment facilities for industrial wastewater (Gulsen and Turan, 2004; Zhang et al., 2005). Reagents dosage requirements were properly assessed by RSM in terms of the relative amount of H_2O_2 required per COD unit, and the molar ratio between H_2O_2 and Fe^{2+} (Figs. 1 and 3). Results were in good agreement with those previously reported for other highly organic loaded wastewater (Hermosilla et al., 2009a; Rivas et al., 2003; Torrades et al., 2011; Zhang et al., 2005). Accordingly, although a 1:1 M ratio between H_2O_2 and Fe^{2+} corresponds to the theoretical optimal stoichiometry for the formation of HO• in a Fenton reaction (Harber and Weiss, 1934), the better operation conditions were provided by ≈1.5 values regardless the initial pH value of the reaction (as shown in Fig. 3), reflecting a net oxidation efficiency loss through parallel reactions (≈33%). Particularly, H_2O_2 is able to reduce Fe^{3+} back to Fe^{2+}, recovering catalyst for further HO• generation, although this process is several orders of magnitude slower than the direct HO• production by Fenton reagents (Hermosilla et al., 2009b; Pignatello et al., 2006).

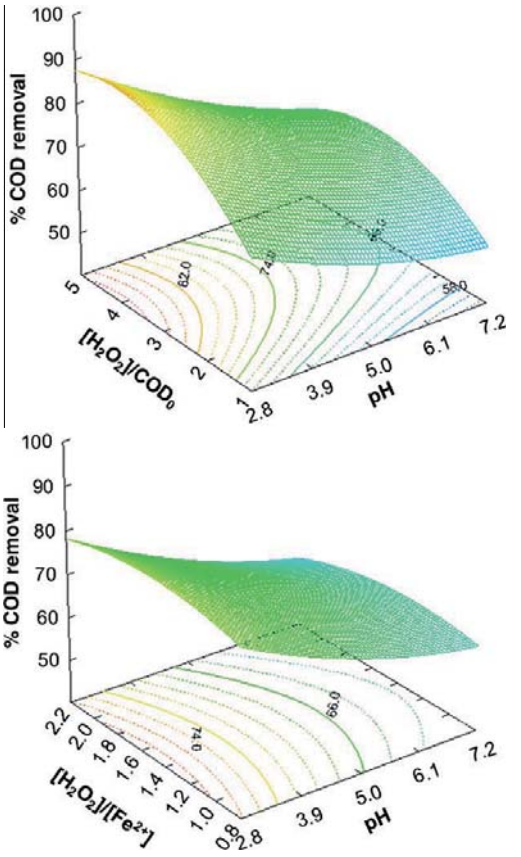

Fig. 1. Response surface and contour plot for the removal of COD from paper mill RO retentate by Fenton treatment considering variable pH and reagents concentrations (T = 25 °C).

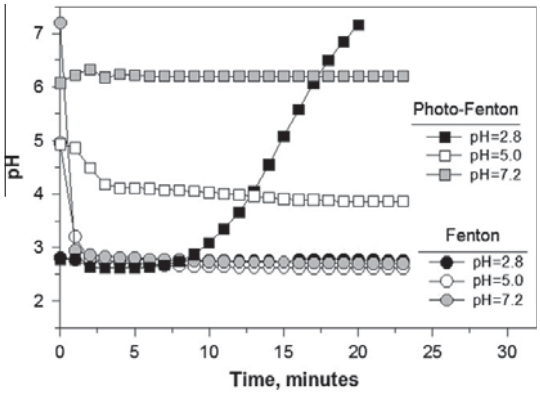

Fig. 2. Evolution of pH from different adjusted initial values along Fenton and photo-Fenton treatment of RO retentate from a paper mill. Reaction variables: T = 25 °C; $[H_2O_2]/COD$ (mg L^{-1}) = 2.125; $[H_2O_2]/[Fe^{2+}]$ = 1.5 (Fenton) and 15 (Photo-Fenton).

The optimal H_2O_2 concentration resulted about 3.8 times the initial COD value, although the additional removal of COD was <5% over 2.8 (Fig. 3). This is 0.675–1.675 times greater than the

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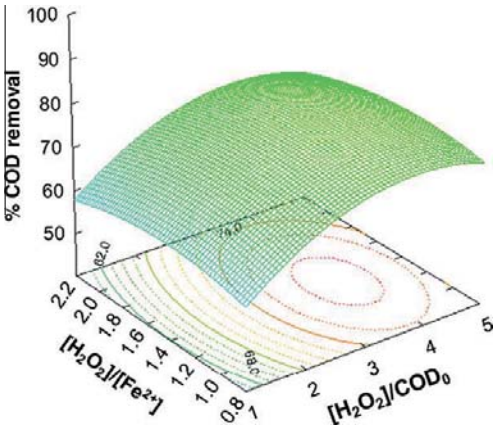

Fig. 3. Response surface and contour plot for COD reduction from paper mill RO retentate by Fenton treatment considering variable reagents concentrations (T = 25 °C).

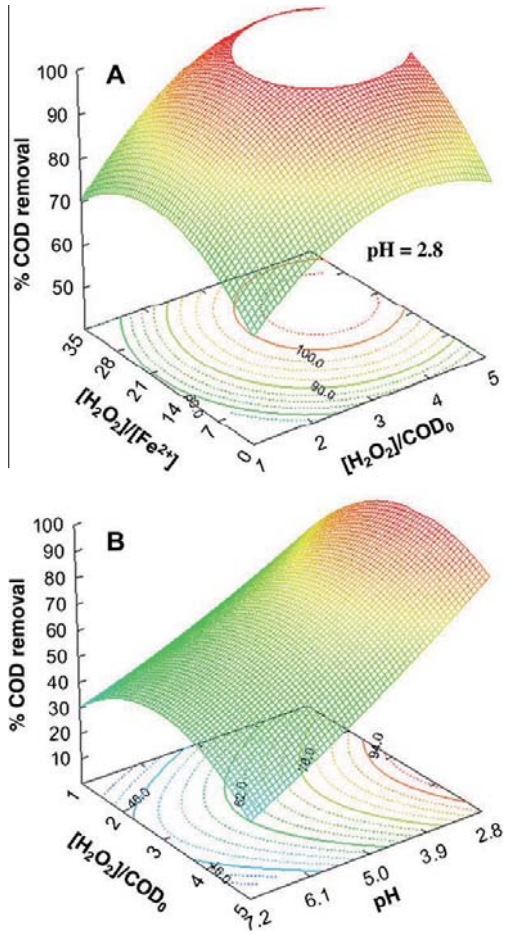

Fig. 4. Response surface and contour plot for COD removal from paper mill RO retentate by photo-Fenton treatment at T = 25 °C and variable concentrations of reagents considering (A) initial pH = 2.8; and (B) variable both pH and H_2O_2 concentration.

theoretical optimal stoichiometrical ratio of 2.125 mg H_2O_2 L^{-1} for every COD mgO_2 L^{-1} (Kim et al., 1997). Previous research reported slightly lower values (2.15–2.40) for the Fenton treatment of phenol (Kavitha and Palanivelu, 2004), brines (Rivas et al., 2003), and black liquor from pulp and paper industry (Torrades et al., 2011); whereas an even higher inefficiency of the added H_2O_2 was found for highly organic-loaded stabilized landfill leachate (Hermosilla et al., 2009b).

Particularly, the use of Fenton treatment for 100% recovered paper newsprint mill effluents has not been reported before. Moreover, available results for the conventional Fenton treatment of wastewater from other paper mills are very limited, and may have not even been optimized. Comparatively, the reduction level of the COD that has been achieved in the performed optimal Fenton treatment of RO retentate from this paper mill is even higher (>80–90%; Fig. 1) than the best reported for other paper mill effluents (30–85%; Catalkaya and Kargi, 2007; Sevimli, 2005; Tambosi et al., 2006). The percentage of TOC removed for the best treatment conditions was 50–60%, which represents a high mineralization ratio for the removed COD, similar to previously reported results for the Fenton treatment of other complex wastewater (Hermosilla et al., 2009b). The fact that coagulation may significantly contribute to remove organic load when a Fenton process is performed at high iron dosages (Kang and Hwang, 2000) may in part explain these very good COD and TOC removal results.

3.2. Photo-Fenton treatment

As Fenton reaction progresses, recalcitrant organic byproducts may be generated, such as some carboxylic acids and fatty acids, as well as organic iron-complexes that hinder the process (Hermosilla et al., 2009a). Particularly, it has been reported that the Fenton treatment of acid fractions from starch degradation is only able to achieve a 3% COD removal, which has been attributed to their organic structure (Amat et al., 2005). These limitations may be widely avoided combining the application of UV-irradiation with the Fenton treatment. As it has been previously reported, a higher treatment efficiency is possible because it enables further treatment of some organics that could not be treated otherwise, and it requires the addition of much less Fe^{2+}, reducing very much turbidity and sludge generation (Hermosilla et al., 2009a; Kavitha and Palanivelu, 2004; Kim and Vogelpohl, 1998; Safarzadeh et al., 1997). The progression of the reaction is further driven by the photo-regeneration of Fe^{2+} from Fe^{3+}, and the breakage of iron complexes (Hermosilla et al., 2009a).

In fact, the optimal photo-Fenton treatment of the sampled RO retentate from the paper mill achieved a total reduction of the initial COD (Fig. 4) and TOC values. The optimal photo-Fenton reaction conditions were addressed at pH = 2.8, $[H_2O_2]/COD > 2.25$, and $[H_2O_2]/[Fe^{2+}] > 10$ (Fig. 4). Particularly, pH resulted to have a greater effect in the applied photo-Fenton process than when performing conventional Fenton treatment, as denoted by the much greater drop in the achieved reduction of the COD at higher pH values than the optimum (compare Figs. 1 and 4). In addition, pH increased naturally to neutral values when the photo-Fenton treatment was performed after adjusting the initial pH value at 2.8 (Fig. 2). Further pH adjustment was not required as fatty organic acids were totally removed.

On the other hand, the performed optimal photo-Fenton treatment required a lower concentration of H_2O_2 to remove more COD than the above-defined optimal conventional Fenton treatment ($[H_2O_2]/COD > 2.8$; Fig. 1); which denotes that Fe^{3+} to Fe^{2+}

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photo-reduction effectively promotes a quicker evolution of the Fenton reaction (Hermosilla et al., 2009a). In turn, the availability of Fe^{2+} becomes the main rate-limiting step of the conventional Fenton process because the regeneration of Fe^{2+} from Fe^{3+} is slower than the consumption of ferrous iron (Hermosilla et al., 2009b; Pignatello et al., 2006); therefore, more H_2O_2 is required to reach the same concentration of HO• that is produced when UV-light is assisting the reaction.

Moreover, the oxidation efficiency of the process (OE = 100·Δϖ COD/available O_2, where "available O_2" matches the theoretical amount of reactive oxygen equivalent to the added H_2O_2; (Bishop et al., 1968) also deteriorates as the reaction further proceeds when Fe^{2+} regeneration by H_2O_2 becomes predominant (Hermosilla et al., 2009b). Accordingly, considering the theoretical stoichiometrical H_2O_2 concentration of 2.125 times the COD value, it results that OE is significantly greater for photo-Fenton (OE = 0.78) than for conventional Fenton treatment (OE = 0.64) at pH = 2.8. Finally, a much higher requirement of Fe^{2+} addition will further imply an associated higher cost for iron sludge disposal after performing the conventional Fenton treatment of RO retentate. In fact, less iron sludge generation has been reported previously when optimizing Fenton and photo-Fenton treatments of landfill leachate (Hermosilla et al., 2009b) and in this case $[H_2O_2]/[Fe^{2+}]$ ratio may be higher than 30 (Fig. 4).

3.3. TiO_2-photocatalytic treatment

Although the reduction of the COD seemed to be almost maximized during the first hour of treatment, as reported previously in other similar trials (Dialynas et al., 2008), it stepped up further from 90 min onwards (Fig. 5). During the first 10 min of treatment (UV-lamp switched off) part of the COD is adsorbed in TiO_2. It was measured that 25, 75 and 95 mgO_2/L of COD were adsorbed for 1, 5 and 10 g/L dosages of TiO_2 respectively. After switching the lamp on, easily oxidizable organics were removed; and in a second stage, organic matter was eliminated at a much slower rate (up to ≈60 min). As easier-to-oxidize byproducts are generated from the treatment of more recalcitrant chemicals, a higher COD removal can be achieved. Similar successive stages may alternate prolonging the process indefinitely, so a 5 h treatment was set as a reasonable reference to compare results. Further treatment did not seem to add significant reduction of the COD for the investment of such an extra reaction time and cost (Fig. 5).

The overall efficiency of the process was strongly influenced by the dosage of TiO_2 (Figs. 5 and 6), as it has been reported previously (Chang et al., 2004; Tanaka et al., 1999). The degradation of organics is improved until an excessive catalyst dosage causes a shadow effect interfering with the transmission of UV light, so electron–hole pairs generation cannot effectively occur (Catalkaya and Kargi, 2007; Chang et al., 2004). An optimum dosage of 10 g L^{-1} of TiO_2 was found to maximize the removal of COD (35–40%) and TOC (30–35%) after a 5-h TiO_2-photocatalytic treatment of the sampled RO retentate (Fig. 6), as it has been previously reported for the equivalent treatment of lignin powder (Chang et al., 2004). Although the removal of COD is not much better (≈5%) than using 5 g$[TiO_2]$ L^{-1}, the mineralization of the organic fraction was much enhanced (>2 times). These COD removal ranking results are similar to those reported comparing TiO_2-photocatalytic and solar photo-Fenton treatments of effluents from board industry (Amat et al., 2005).The shown limited efficiency of TiO_2-photocatalyisis was attributed to the lower oxidative power this treatment developed in comparison to the previously applied Fenton processes, as reflected by the evolution of the measured redox potential along the reaction time. While redox potential raised pretty quickly during the first 2 min of Fenton and photo-Fenton processes from an initial value of 400 RmV to final values of 530 and 550 RmV, respectively; its evolution was more progressive along the photocatalytic treatment, beginning at −100 RmV, and still increasing more or less linearly after reaching 55 RmV after a 3-h trial.

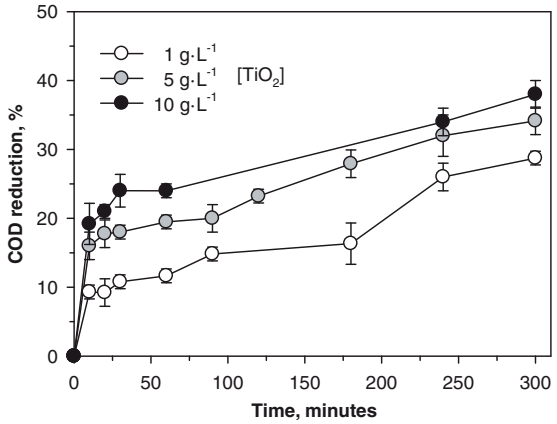

Fig. 5. Reduction of the COD along reaction time when performing the treatment of RO retentate from a newsprint paper mill by TiO_2-photocatalysis at different concentration levels of the catalyst (T = 25 °C, initial natural RO-retentate pH value after the addition of the catalyst = 7.2).

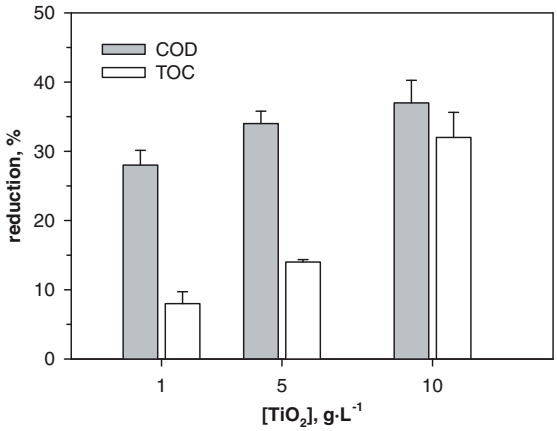

Fig. 6. TiO_2-photocatalysis efficiency in the treatment of RO retentate at different concentration values of the catalyst (T = 25 °C, initial natural RO-retentate pH value after the addition of the catalyst = 7.2, reaction time = 300 min).

Beyond these overall poorer oxidative results, it has furthermore been highlighted that the photocatalytic degradation of organics mainly affected those pollutants that are more reluctant to biological degradation, thus enhancing much the biodegradability of wastewater (Amat et al., 2005; Yeber et al., 2000). Particularly, it has been shown that it may be able to reduce over the 30% content of high molecular weight compounds present in cellulose bleaching effluents (Yeber et al., 2000). Therefore, TiO_2-photocatalysis may be considered as an interesting pre-oxidation step preceding biological treatment of paper industry wastewater. In fact, biodegradability was improved along the TiO_2-photocatalytic treatment of RO retentate, even achieving close figures to those developed by ethylene glycol (≈100% COD removal) when 10 g L^{-1} of TiO_2 were used (Fig. 7).

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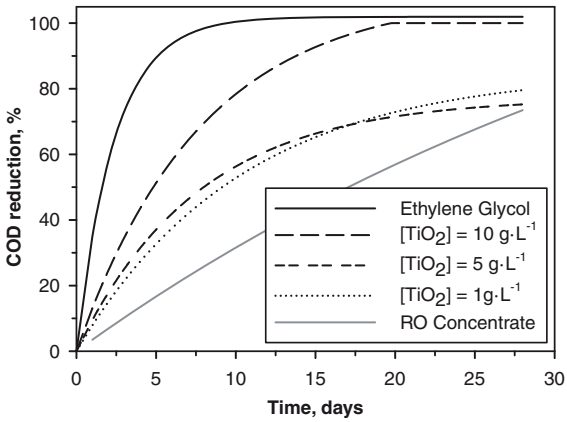

Fig. 7. Biodegradability evolution along the optimal TiO_2-photocatlaytic treatment of RO retentate from a newsprint paper mill.

3.4. Some considerations regarding the cost of the treatments

Considering a first tentative economical assessment of the cost of the tested treatments, it could be easily understood that, whereas the conventional Fenton treatment implies a higher cost in terms of chemical reagents, which will furthermore imply an associated higher cost for iron sludge disposal as well; the photo-Fenton treatment requires a higher cost in terms of energy consumption. In short, a first estimation of the treatment cost in terms of reagents and energy implied at lab scale resulted in about the same order of magnitude for both optimal Fenton (4.17 $/m^3; calculated as described in Esplugas et al., 2002) and photo-Fenton (3.63 $/m^3) treatments yielding a 70% COD removal; resulting the latter much interesting if we consider that it is even able to produce a 100% reduction of the COD, its much lower associated cost for iron sludge disposal, and the potential use of a solar source of radiation to substitute UV lamps and save from the associated cost of energy whenever possible.

On the other hand, TiO_2-photocatalytic treatment showed more than a half lower COD and TOC removal figures at best, requiring very long treatment times, and therefore increasing much the use of UV-lamps and the associated cost of energy (up to 74.80 $/m^3 for a 33% COD reduction). As much longer time (up to 5 h) was required for producing the same COD removal target than photo-Fenton (5 min), photocatalysis may could only represent an interesting treatment alternative whenever it would be possible to use the sun as an alternative source for radiation, which application may be further limited for high effluent flows (3000 m^3/day) by an increased residence time and its associated operational cost.

4. Conclusions

- The photo-Fenton process was the most effective among the tested treatments for RO retentate from a paper mill, achieving the total reduction of COD and TOC. Further-more, it was cheaper than conventional Fenton at higher COD reduction treatment thresholds.
- In addition, although better results were produced when the initial pH value was pre-adjusted to 2.8, Fenton processes were able to achieve acceptable high COD reduction results (>60%) without adjusting the initial pH value of the solution, which is close to neutral.
- TiO_2-photocatalysis increased the biodegradability of the highly concentrated RO retentate enough to consider its combination with a posterior biological step in order to achieve an almost total reduction of the COD. A solar version of this process might reduce much the high energy cost that has been associated to this treatment.

Acknowledgments

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PAPER IV

N. Merayo, D. Hermosilla, B. Jefferson, A. Blanco

Alkalinity influence on photo-assisted processes efficiency and catalyst behaviour

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Alkalinity influence on photo-assisted processes efficiency and catalyst behaviour

Noemí Merayo[a], Daphne Hermosilla[a*], Bruce Jefferson[b], Ángeles Blanco[a]

[a] *Department of Chemical Engineering, Complutense University of Madrid, Facultad de Ciencias Químicas, Ciudad Universitaria s/n, 28040 Madrid, Spain.*

[b] *Cranfield Water Science Institute, Department of Environmental Science and Technology, Cranfield University, Bedfordshire MK43 0AL, UK.*

[*] Corresponding author:
Tel.: +34 91 394 4645; fax: +34 91 394 4243
E-mail address: dhermosilla@quim.ucm.es (D. Hermosilla)

Abstract

This research unravels the influence of carbonates on TiO_2-photocatalysis and photo-Fenton using Fe^0 as catalyst. The aggregation behavior of each catalyst was monitored under different reaction conditions in order to assess the effect of carbonates on their performance, whose presence drastically reduced the efficiency of photocatalysis because of the aggregation tendency of the catalyst, which reduced the amount of adsorbed pollutant, and consequently limited the treatment efficiency. The addition of carbonates to the photo-Fenton process did not produce strong catalyst aggregation. Therefore, oxidation-reduction reactions on the catalyst surface were not much reduced, and the efficiency of this process did not resulted as affected as the efficiency of photocatalysis.

Keywords: carbonate; lignin; photocatalysis; photo-Fenton; zero-valent iron.

1. Introduction

Lignin is the chemical compound responsible for the union of cellulose fibers. During the pulp production process, lignin is dissolved aiming to release the fibers. As a consequence, lignin is one of the main contributors to chemical oxygen demand (COD) and color in the effluents of virgin-fiber pulp mills. In addition, these effluents are also characterized by high alkalinity values because calcium carbonate, mainly, and other inorganic compounds are added as fillers in the production process [1].

Lignin is a polymer formed by aromatic units, mainly phenolic, and its decomposition may produce toxic by-products [2]. Conventional biological wastewater treatments cannot appropriately mineralize lignin because it is highly resistant to bacterial attack [3]; but advanced oxidation processes (AOPs) may be a good alternative for the successful removal of bio-recalcitrant toxic contaminants [2, 3, 4] because they can break complex organic structures down into simpler more biodegradable ones [5]. These processes degrade pollutants thanks to the generation of hydroxyl radical (OH·) [6] which is able to effectively oxidize the organic substances present in wastewater [7].

Good efficiencies have previously been reported treating lignin by TiO_2 photocatalysis at basic pH [3, 4]. The addition of carbonates has reported increase of the TiO_2 photocatalysis efficiency only during the treatment of acid solutions presumably thanks to the rise of the pH to neutral or even slightly basic values [8-10]. In fact, the adsorption of anions on the surface of the positively-charged catalyst may hinder the adsorption of the pollutants under acid pH conditions [11]. On the other hand, higher [12, 13] to slight [14-16] reductions of the efficiency of TiO_2 photocatalysis have also been reported at different initial pH values of the treated solutions.

The positive or negative effects that have been attributed to the presence of carbonates have been related to their concentration in the treated wastewater [10] or to charge differences in the case of dyes being treated [17]. Other authors reported an inhibitory effect of carbonates when treating both cationic and anionic dyes, addressing a higher inhibitory effect under neutral pH conditions rather than basic [18]. The reduction of the treatment efficiency has been attributed to the modification of the pH that is promoted after the addition of carbonates [19]; although it has also been reported when performing the treatment at a fixed pH value and explained in terms of the scavenger effect of carbonate over OH· [20]. Finally, no inhibitory effect was detected by Wang et al. [21] although the adsorption of the dye on TiO_2 surface was reduced by the presence of carbonates in the solution.

Fenton's reagent has also been used to degrade lignin in effluents from pulp mills [22] and synthetic lignin solutions [2], achieving its complete degradation under acid pH conditions; although, as it was expected, this treatment has reported poor results when it was performed at basic pH values [2,23]. The combination of UV light and the use of zero valent iron (Fe^0) as heterogeneous catalyst avoids the use of iron salts and prevents the generation of iron sludge in the process. Even though this catalyst can be dissolved reacting in a homogeneous process at acid pH, the generated iron sludge is generally low in comparison to the traditional process [24].

In general, the Fenton process is highly influenced by the pH of the solution. Particularly, pH=2.8 has previously been addressed as the optimum value to perform this treatment [25]. Therefore, the addition of carbonates, which actually increases the pH of the solution, would be expected to reduce its efficiency. In fact, the inhibitory effect of the presence of carbonates was reported in the Fenton treatment of nitrophenols even fixing pH=5.2 [26]. In addition, the inhibitory effect promoted by the presence of carbonates when treating dyes by photo-Fenton has been explained by the aggregation of dye molecules in the presence of inorganic anions. As a consequence, these aggregates are attacked by OH· with more difficulty [27]. On the other hand, the use of Fe complexes (Fe-EDDs) as catalyst in a photo-Fenton like process did not resulted very much influenced by the presence of carbonates [28], attributed to the particular reaction mechanism of this catalyst.

The reaction of CO_3^{2-} and HCO_3^- with OH· generates $CO_3^{\cdot-}$ and $HCO_3^{\cdot}$, both which hold a lower oxidation power than OH· itself, thus reducing the efficiency of the process. Nevertheless, the kinetics of these reactions are typically slower than the kinetics of the reaction between OH· and organic compounds. Therefore, the potential scavenger effect of these anions may not be significant unless the amount of them in the solution would be high enough in comparison to the amount of organic compounds [29].

Furthermore, the addition of anions to the reaction medium increases the ionic strength of the solution, which favors the spontaneous aggregation of particles [30]. As a consequence, the inhibitory effect of a high alkalinity might be attributed to the formation of organic compounds aggregates, as well as the aggregation of heterogeneous catalysts. In fact, the potential role of catalyst aggregation has not been considered yet within the assessment of the unclear influence of alkalinity on the performance of photo-assisted processes, herein, TiO_2 photocatalysis and photo-Fenton

using Fe^0, which has rather been reported contradictory to date. The main objective of this essay is to unravel the effect of alkalinity on heterogeneous catalyzed photo-assisted processes.

2. Materials and methods

2.1. Materials and analytical methods

Synthetic wastewater was prepared using alkali lignin from Sigma Aldrich (Poole, UK). Hydrogen peroxide (35% w/w), sulfuric acid, sodium hydroxide, and sodium bicarbonate were used from Fisher Scientific (Loughborough, UK). TiO_2 (Aeroxide® TiO_2 P25 Degussa) and Fe^0 microspheres from BASF (Ludwigshafen, Germany) were used to perform the experiments.

COD was measured using Spectroquant® cell test kits from VWR (Lutterworth, UK) with a NOVA 60 spectrophotometer (Merck, Nottingham, UK). H_2O_2 concentration was determined by the titanium sulfate spectrophotometric method [31]. Lignin and its degradation products were determined by high performance liquid chromatography (HPSEC) carried out using an HPLC (Shimadzu VP Series, Shimadzu, Milton Keynes, UK) with UV detector set to 254 nm. 0.01 M sodium acetate at a flow rate of 1 ml·min^{-1} was used as mobile phase. The column was a TSK–gel G3000SW of 7.5 mm (ID) × 30 cm (Tosoh BiosepGmbH, Stuttgart, Germany). An UV absorbance chromatogram (arbitrary units) against time (min) was generated each experimental run. The measurement of the molecular weight of the compounds present in the solution allows identifying the breakage of lignin polymer into smaller molecules, even if they have the same structural characteristics.

The behavior of each catalyst was assessed using an M500L focused beam reflectance measurement (FBRM) probe manufactured by Lasentec (Mettler Toledo, Seattle, WA). The FBRM instrument reports on-line measurement of the chord length distribution of a solution. The measurement is based on the time duration of the backscattered light from the particles. Each detected particle is counted, and thousands chord length measurements are collected per second, producing a histogram in which the number of observed counts is sorted in several chord length bins over the range of 0.5 to 1000, or 2000 μm [32].

2.2. Experimental procedures

2.2.1. Collimated beam apparatus

UV experiments were all conducted in a Wedeco AG bench scale quasi-collimated beam apparatus (Herford, Germany) fitted with four 30-W low-pressure Hg-lamps that emit monochromatic light at 254 nm. A warm-up time of 30 min was allowed to ensure consistent light output before irradiating the solution. A volume of 250 mL of the solution to test was placed in a Petri dish 22 cm away from the light source, and stirred with a magnetic device along each trial. UV irradiance from the collimated beam was determined to be 22.6 $W \cdot m^{-2}$ by the uridine actinometry methodology described by von Sonntag and Schuchmann [33].

2.2.2. UV/TiO_2

TiO_2 photocatalytic treatment was performed on 250 mL samples of a 300 $mg \cdot L^{-1}$ lignin solution. Optimum COD removal was reported at a dose ratio of 0.014 $gTiO_2 \cdot mg^{-1}$COD [34]. Considering this and the initial concentration of lignin in the solution, the corresponding optimum dose would be 7 $gTiO_2 \cdot L^{-1}$. A lower (5 $gTiO_2 \cdot L^{-1}$) and a higher (9 $gTiO_2 \cdot L^{-1}$) dose were also tested to optimize the treatment of lignin.

Experiments adding $NaHCO_3$ in doses ranging from equivalent 100 to 750 $mg \cdot L^{-1}$ of $CaCO_3$ were performed to assess the influence of alkalinity, which was measured as mg of $CaCO_3$ per liter, so it would also be alternatively named as carbonate in generical terms. A batch of trials was performed to assess the influence of pH changes on the treatment. 750 $mg \cdot L^{-1}$ of $CaCO_3$ was selected as the reference for pH modifications. pH adjustment adding sulfuric acid and sodium hydroxide was done when required. Samples were periodically withdrawn (5, 10, 15, 30, 60, 120 and/or 720 min) and filtered through a Millex-HA 0.45 μm syringe filter to separate the suspended TiO_2 prior to analysis.

2.2.3. UV/Fe^0/H_2O_2

Photo-Fenton process was performed following the same procedure than TiO_2 photocatalysis but adding Fe^0 and H_2O_2 to the solution instead of TiO_2. The optimum H_2O_2 dose to was selected based on the theoretical stoichiometrical relation between initial COD and the calculated amount of H_2O_2 that would be required to totally oxidize the organic matter in the solution, that is, 2.125 [35]. In addition, a higher (3.125) and a lower (1.125) rate were also tested to verify whether the optimal treatment of lignin solution was actually achieved. Using Fe^0 instead of Fe^{2+} salts as catalyst avoided the addition of more salts along the trials with modified alkalinity. The optimum molar

relation between the initial amounts of H_2O_2 and Fe^0 was 60, which was selected based on previous results [36]. Finally, NaOH was added to the samples to precipitate iron and stop the reaction before filtrating and analyzing them. H_2O_2 final concentration contribution to COD value was corrected according to Hermosilla et al. [24].

Experiments adding $NaHCO_3$ in doses ranging from equivalent 250 to 1000 $mg \cdot L^{-1}$ of $CaCO_3$ were performed to test the influence of alkalinity on this process. As well as in the case of photocatalysis, some extra trials were performed to assess the influence of pH using 750 $mg \cdot L^{-1}$ of $CaCO_3$ as the reference for pH modifications.

2.3. Statistical analyses

One-way ANOVAs were run (SigmaPlot 11, SPSS Inc.) to determine the significant level of differences among experimental runs. *Post hoc* all pairwise comparisons were performed using Tukey's test ($P<0.05$).

3. Results and discussion

3.1. The influence of alkalinity on TiO_2 photocatalysis

The addition of 7 $g \cdot L^{-1}$ of TiO_2 to the objective lignin solution reported a significant increase in the reduction of the COD of about a 10% in comparison to 5 $gTiO_2 \cdot L^{-1}$; and there were not significant differences between 7 and 9 $gTiO_2 \cdot L^{-1}$ dosages (Figure 1). Therefore, 7 $gTiO_2 \cdot L^{-1}$ resulted the optimum dosage for this treatment, which is in agreement with previously reported results [34].

TiO_2 photocatalysis showed a drastic decrease of its efficiency depending on the added amount of $NaHCO_3$; that is, ≈80% COD removal was achieved without modifying alkalinity, whereas just 30-50% COD reductions were obtained when this salt was added (Figure 2). Furthermore, lignin removal was initially caused by its adsorption on the surface of TiO_2, so COD reduction under dark conditions resulted about the 70% after five contact minutes. Thereafter, the removal of lignin was caused by the ongoing oxidation process. Catalyst aggregation was observed in presence of $NaHCO_3$ or NaOH (Figure 3), which implied a reduction of the available catalyst surface; so the efficiency that was associated to adsorption consequently resulted reduced as well.

At low carbonate concentration, 0-100 $mg \cdot L^{-1}$ of $CaCO_3$, an initial high COD removal, caused by the initial adsorption of lignin on the surface of the catalyst, was followed by no further COD reduction, and no desorption from catalyst surface.

Therefore the amount of molecules in the solution was reduced and the remained molecules showed lower molecular weight than those present in the untreated solution (Figures 4A and 4B).

Under higher carbonate addition, 250-750 $mg \cdot L^{-1}$ of $CaCO_3$, the photocatalytic treatment promoted the same initial high COD removal, but followed by a slight decrease thereafter. This higher addition of carbonate resulted in an increase of the number of molecules in the solution, with a wide range of sizes (Figure 4C). Some lignin, together with intermediate compounds, was desorbed from TiO_2 surface during reaction. Therefore, the amount of molecules in the solution and the remaining COD were limitedly increased along treatment.

Nevertheless, when these photocatalytic trials in the presence of carbonate were prolonged up to accumulate a total applied UV fluence of 97632 $mJ \cdot cm^{-2}$ (Figures 4B and 4C), an even greater COD reduction was achieved than when previous typical 16272 $mJ \cdot cm^{-2}$ were applied (Figures 1-2). In summary, a 78% COD reduction was obtained in the presence of 750 $mg \cdot L^{-1}$ of $CaCO_3$ when this very high UV fluence was accumulated; whereas a 95% COD removal resulted when 100 $mg \cdot L^{-1}$ of $CaCO_3$ were added to the solution. The presence of a higher carbonate concentration caused the generation of more intermediate products with higher molecular weight, which would require a greater degree of oxidation. In short, the reduction of the efficiency caused by the presence of carbonates can be counterbalanced by the increase of the UV fluence applied in the treatment, although higher carbonate concentration would be expected to achieve lower COD reduction values at the same treatment conditions (Figure 4).

The addition of carbonate caused pH to change in the solution, which may affect the efficiency of the process. TiO_2 photocatalysis did not show statistical differences between the results obtained increasing the pH either adding carbonate or NaOH (Figure 5); although experiments with NaOH reported lower COD removal. In fact, HPSEC analyses showed similar structures for the generated intermediate products whether obtained when the lignin solution was treated in the presence of carbonate or NaOH (Figures 4C and 4D, respectively).

The addition of NaOH to the solution increased the aggregation of the TiO_2 catalyst. That is because the semiconductor behavior of TiO_2 assisted the transference of electrons, which were released from adsorbed OH^- due to a redox reaction [37], through TiO_2 structure, which is an acceptor; thus reducing the catalyst's surface charge and repulsion forces, therefore favoring the aggregation of particles. A greater degree of

aggregation was detected in the experiments adding NaOH (Figure 3) because the resulting water ionic strength is higher than in alkaline solutions. In addition, spontaneous aggregation is also more favored in the presence of NaOH than when carbonates are added [38]. On the other hand, the scavenger effect of HCO_3^-/CO_3^{2-} did not result very important, being its electron donor effect much lessened.

In addition, in order to understand the role of pH, sulfuric acid was added to decrease the pH down to the initial value of the lignin solution (pH=6.5). When sulfuric acid was so added to the solution together with carbonate, the reduction of the COD increased a little (5-10% depending on the applied UV fluence; Figure 5). This can be explained by the fact that competition for reactive sites on the surface of TiO_2 is lower at neutral pH values; therefore, higher treatment efficiency may be expected [11]. Nevertheless, the greatest COD reduction reached without any salts addition was not achieved. Therefore, although lowering the pH had an overall positive effect, catalyst aggregation did not reversed, so it was not possible to achieve the same result.

In short, trials performed in the presence of NaOH produced worse results than those using alkaline lignin solutions. The presence of these compounds, $NaHCO_3$ or NaOH, decreased the efficiency of the process due to the resulting irreversible aggregation of the catalyst in their presence; thus reducing available catalyst surface for the reaction in comparison to those essays that were performed without any addition of salts.

3.2. *The influence of alkalinity on Fe^0-photo-Fenton process*

Regarding the optimization of H_2O_2 dosage, the ratio $[H_2O_2]_0/COD_0$=1.125 addressed the lowest COD removal: 20-25%; whereas ratios of 2.125 and 3.125 produced 40-50% reductions of the COD (Figure 6). As differences between the latter were not statistically significant, the ratio $[H_2O_2]_0/COD_0$=2.125 was selected optimum.

The optimal photo-Fenton treatment addressed a COD removal <50% in the absence of carbonate (Figure 7), which was pretty lower than the results produced by TiO_2 photocatalysis because the natural pH of the solution (≈6.5) is far from optimum value to perform a photo-Fenton treatment, which is 2.8 [25, 39] because of the solubilization of iron species at pH<4 [40].

The presence of carbonate showed little influence on the efficiency of the photo-Fenton process. COD reduction after a 2 hours treatment resulted similar whether carbonate concentration was null or 250 $mg \cdot L^{-1}$ of $CaCO_3$. In addition, differences with

COD reductions at higher carbonate addition, which resulted 5% lower, were much smaller than in photocatalysis (Figure 2 and 7).

The behavior of Fe^0 was monitored in order to find out whether carbonate had any influence on its performance and, consequently, on treatment efficiency. The presence of carbonate produced certain low degree of aggregation (FBRM measurement, data not shown), which might have been responsible of the small decrease of COD removal addressed in the presence of carbonates (Figure 7).

After a steep initial increase, COD removal slightly decreased at the beginning of the experimental process when higher doses of carbonate, 750 and 1000 $mg \cdot L^{-1}$ of $CaCO_3$, were added, thereafter proceeding with a continuous much slower increase of the degradation of the organic load of the solution; meaning that, the whole reaction evolution resulted slower because of this catalyst aggregation phenomena.

A study of the structure of the molecules involved on the treatment was also conducted using HPSEC analyses (Figure 8). The high molecular-weight lignin-polymer was broken down by the photo-Fenton treatment from the very first minutes of the process, generating intermediates with lower molecular weight. There were not detected differences in the formation of intermediate products when varying the amount of carbonate that was added to the solution. The main mechanism degrading lignin was oxidation, and not adsorption. As a consequence, the interference of carbonate is lower, just caused by a small decrease of the available catalyst surface.

Performing again a longer treatment, thus a higher UV fluence of 97632 $mJ \cdot cm^{-2}$ was applied, resulted in a strong improvement of the efficiency of this treatment, even under a high presence of carbonate. Particularly, 92 and 93% COD reductions were achieved when 750 and 250 $mg \cdot L^{-1}$ of $CaCO_3$ were respectively added under these treatment conditions, proving that the presence of carbonate had very little effect on the performance of this treatment. This high COD removal enhancement resulted despite the unfavorably high pH value of the solution.

The experiments assessing the influence of pH on photo-Fenton treatment resulted completely different to photocatalytic ones. A strong decrease of treatment efficiency was addressed when NaOH was used to set the same pH values in the solution that result after the addition of carbonate (Figure 9). In this case, OH^- ions were adsorbed on the surface of Fe^0, avoiding oxidation-reduction reactions on the catalyst's surface and limiting the efficiency of the process. Electron transference was not favored, and OH^- ions kept being adsorbed onto the surface of Fe^0, both increasing repulsion

forces between particles and avoiding the aggregation of the catalyst, although some degree of aggregation can be observed (FBRM measurement, data not shown).

Sulfuric acid was added to a set of trials adding 750 $mg \cdot L^{-1}$ of $CaCO_3$ to the solution in order to set the same pH of the solution when no salts were added (pH=6.5) and check whether the efficiency of the process was improved. Contrarily, it resulted in a greater decrease of its efficiency with respect to the treatment just adding 750 $mg \cdot L^{-1}$ of $CaCO_3$. In conclusion, once carbonate was added to the solution, pH modification towards lower neutral values did not imply better results because the addition of ions to the solution had an important influence on the catalyst's behavior (Figures 5 and 9). It was more likely that the newly added H^+ ions reacted with active sites on the surface of Fe^0, further limiting the available surface for Fenton reaction to occur, therefore reducing the efficiency of the process as in the case of adding NaOH.

4. Conclusions

The TiO_2-photocatalytic treatment of lignin solutions showed a reduction of its efficiency in the presence of bicarbonate that was mainly caused by the adsorption of compounds on the surface of the catalyst.

In the presence of carbonate, TiO_2 showed an important aggregation behavior that reduced the available catalyst surface, ultimately implying losses in the efficiency of the process.

In addition, the presence of carbonate could not be counterbalanced setting the initial pH value of the solution, although some improvement was achieved, mainly because of the irreversible aggregation of TiO_2 particles in relation to salt addition.

The photo-Fenton treatment of lignin solutions using Fe^0 as heterogeneous catalyst showed a slight influence of the presence of carbonate on the efficiency of the process, which was mainly based on the oxidative process running on the catalyst's surface.

Fe^0 did not suffer great aggregation in the presence of carbonate, and available catalyst surface did not resulted highly reduced, although it involved a slight reduction of process efficiency.

pH modification to the natural value of the solution (6.5) did not improve the efficiency of the photo-Fenton process in the presence of high contents of carbonate. Contrarily, the additions of ions to the solution negatively affected the process.

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Figure legends

Figure 1. Optimization of the catalyst dose in the TiO_2 photocatalytic treatment of a 300 $mg \cdot L^{-1}$ lignin solution in relation to UV fluence. Letters (a,b) identify statistically significant differences in the results at the end of the process (Tukey's test, $P < 0.05$).

Figure 2. Carbonate concentration influence on the removal of the COD along the TiO_2 photocatalytic treatment of a 300 $mg \cdot L^{-1}$ lignin solution in relation to UV fluence. Letters (a,b,c) label statistically significant differences in the results at the end of the process (Tukey's test, $P<0.05$).

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Type of Article:
Initial removal of the lignin by TiO_2 photocatalysis was due to the adsorption on the catalyst surface, which was strongly reduced in the presence of carbonates. Aggregation of the Fe^0 catalyst was lower than for TiO_2 catalyst. In photo-Fenton process the oxidation of lignin through intermediates with lower molecular weights was slightly affected by the presence of carbonates.

Influence of alkalinity on the efficiency of photo-assisted processes and on the catalyst's behavior

Noemí Merayo, Daphne Hermosilla*, Bruce Jefferson, Ángeles Blanco

Chem. Eng. Technol. **20XX**, *XX (X)*,
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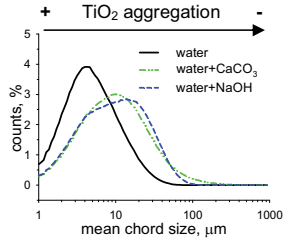

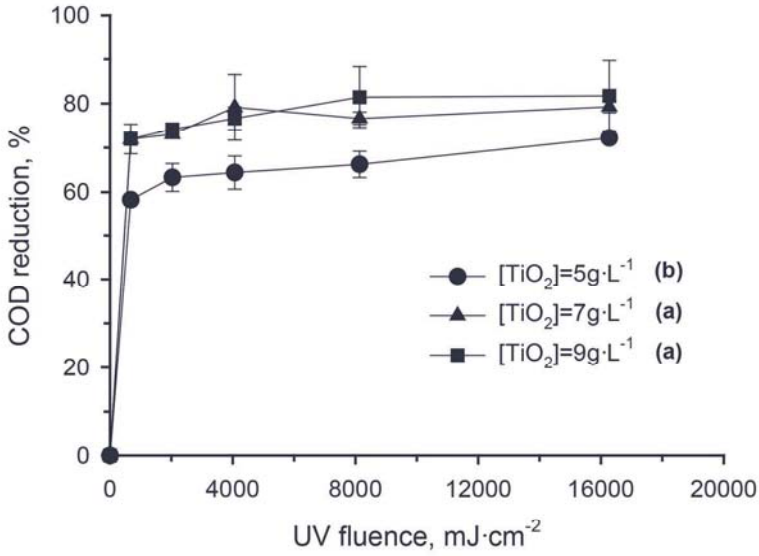

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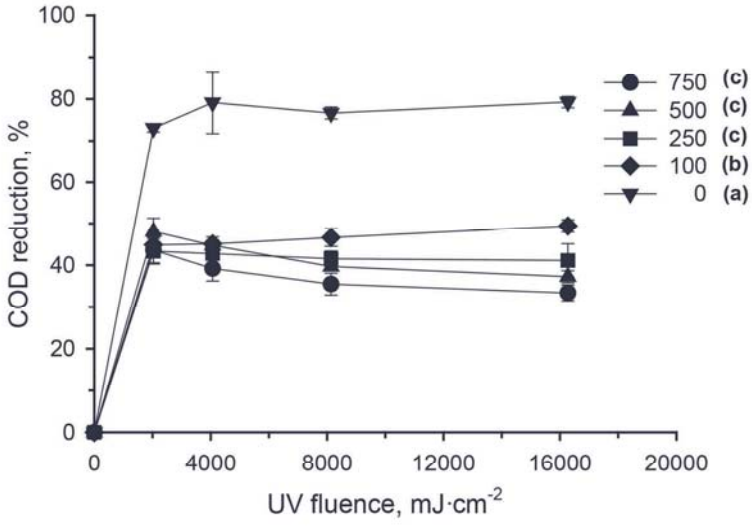

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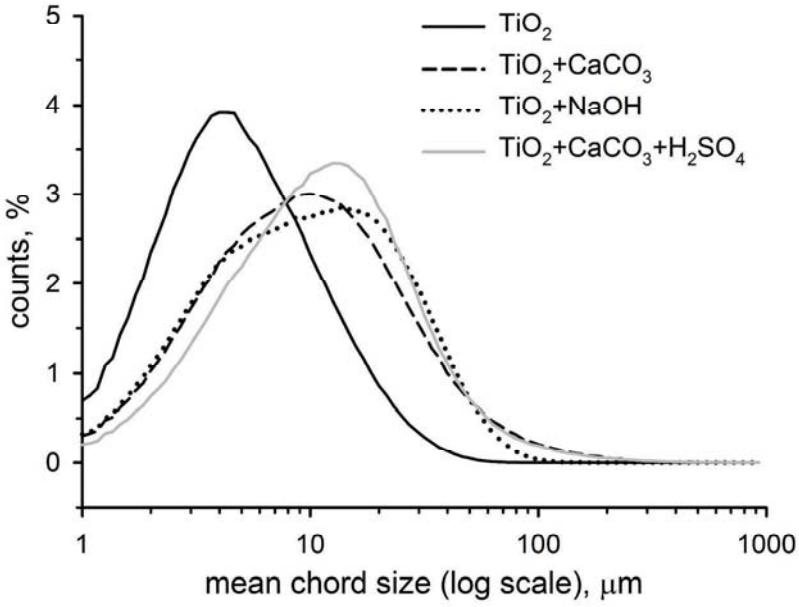

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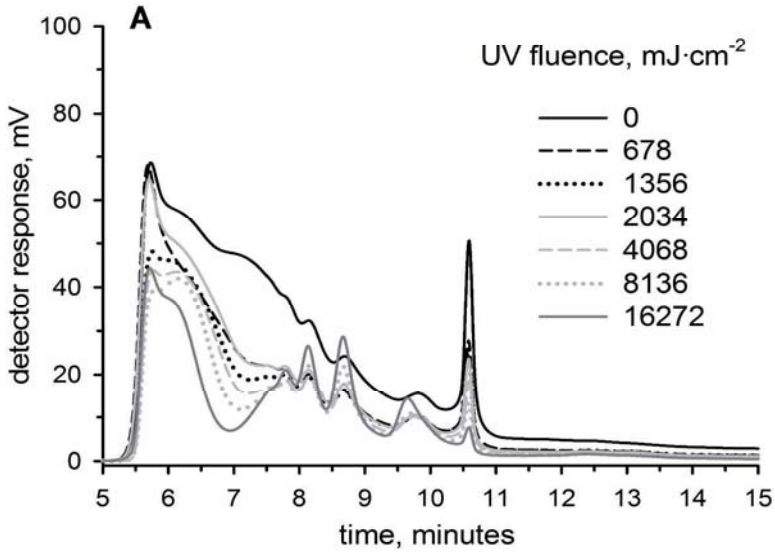

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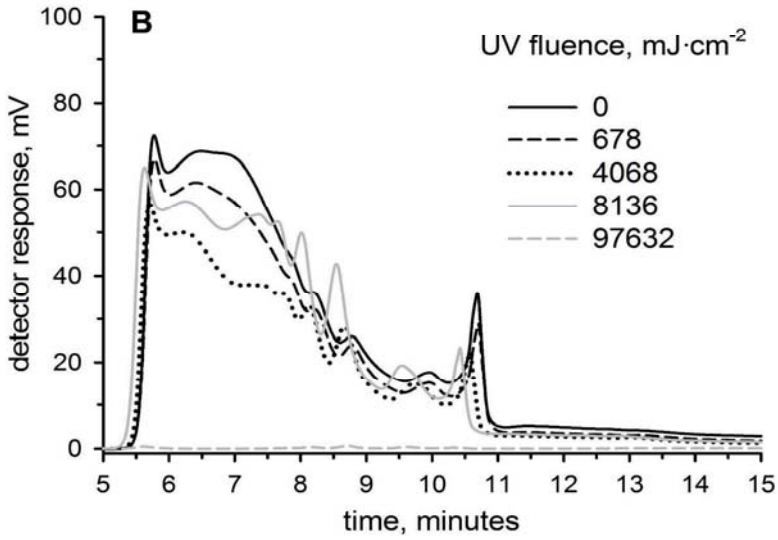

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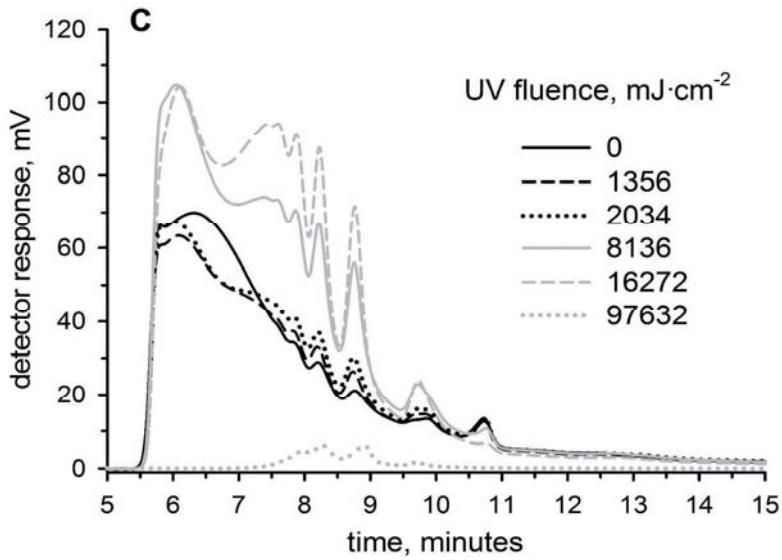

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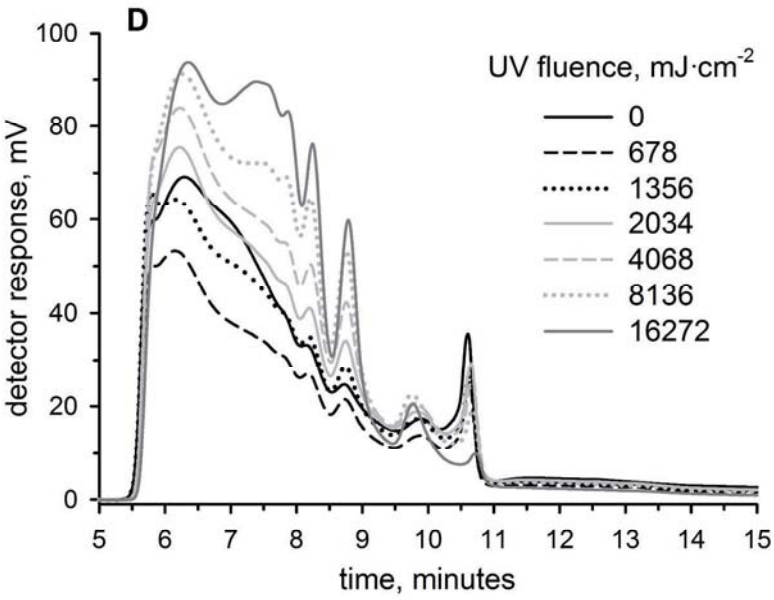

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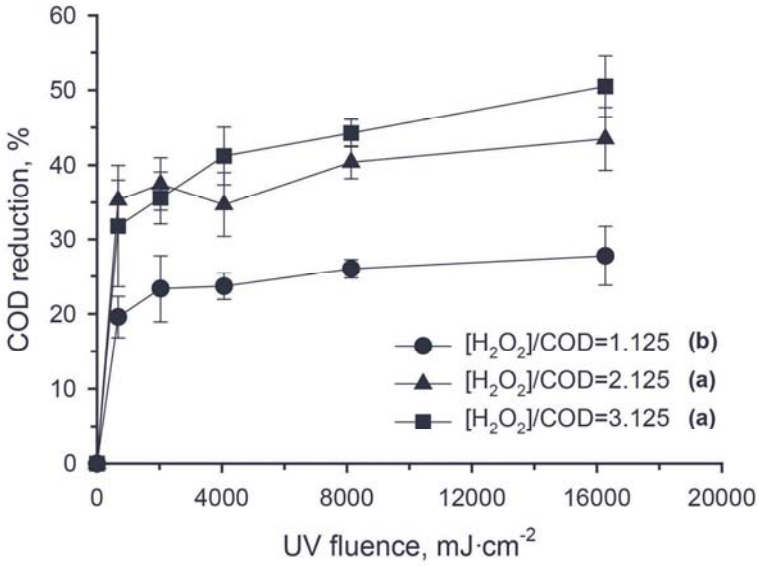

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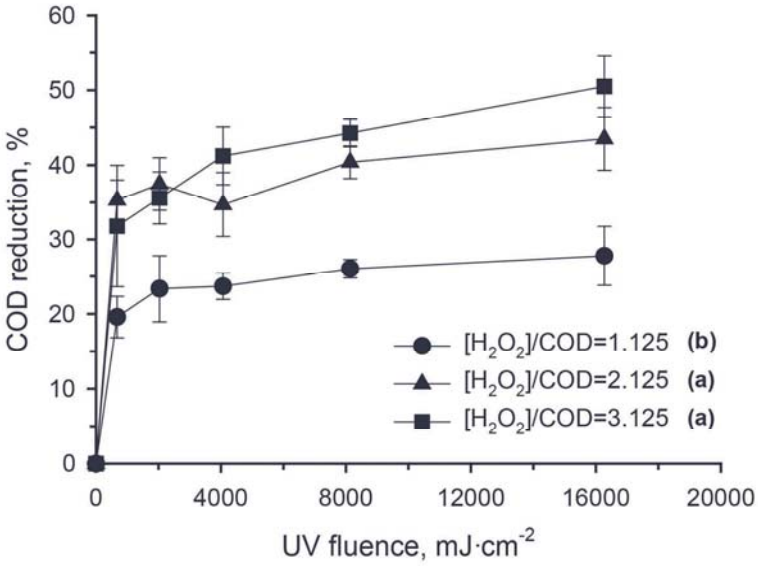

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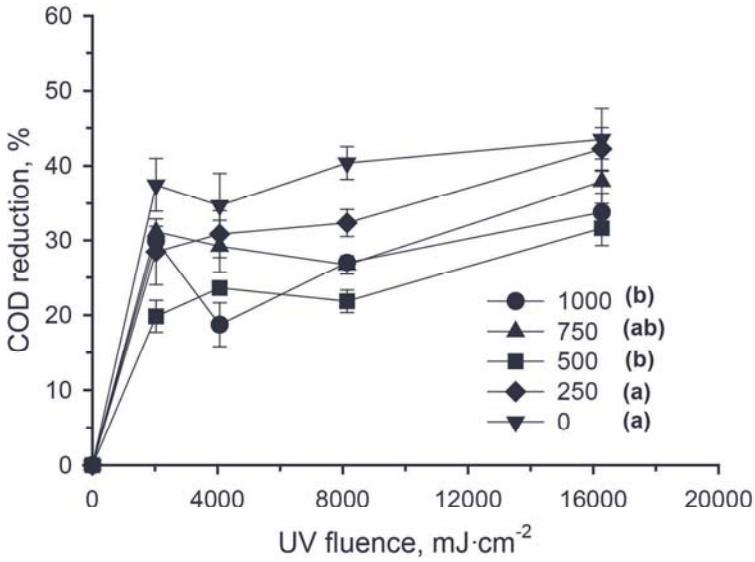

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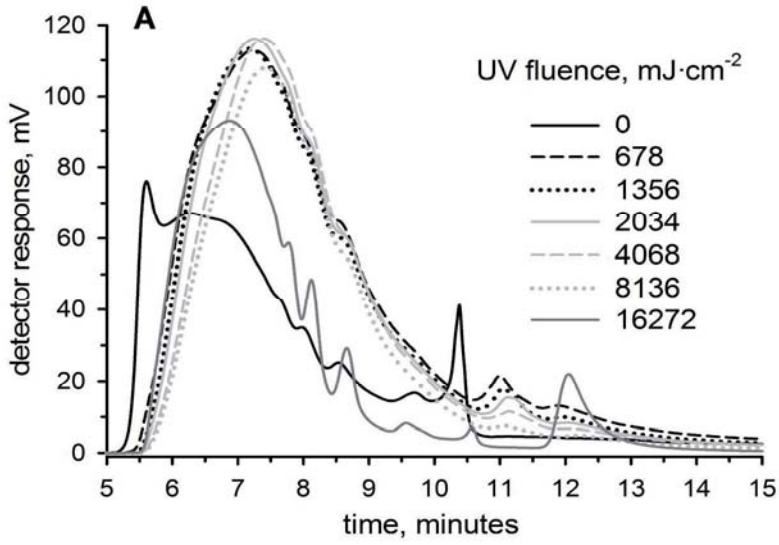

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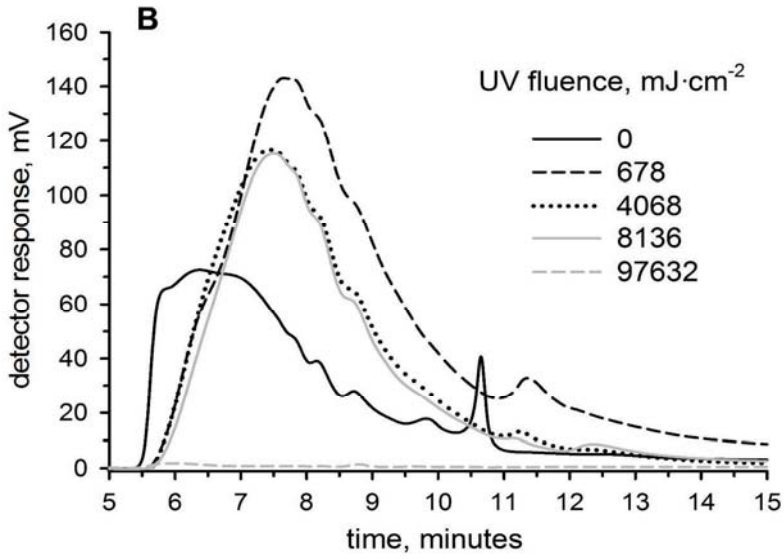

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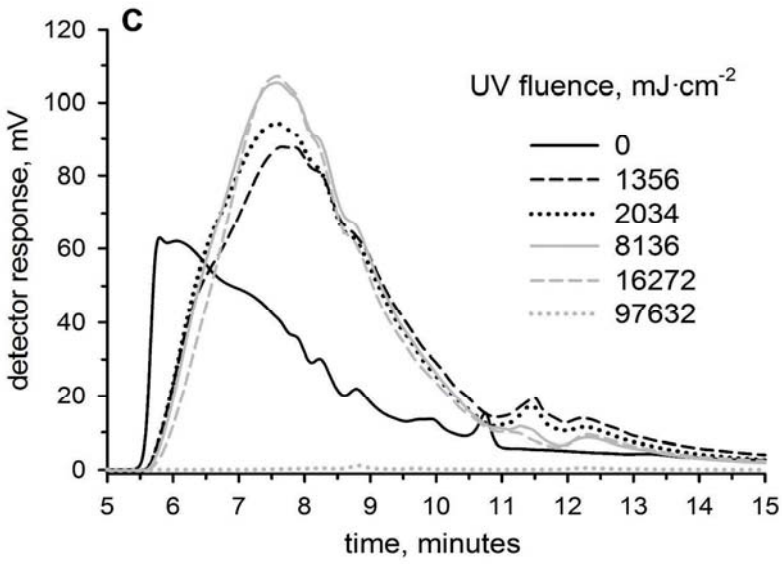

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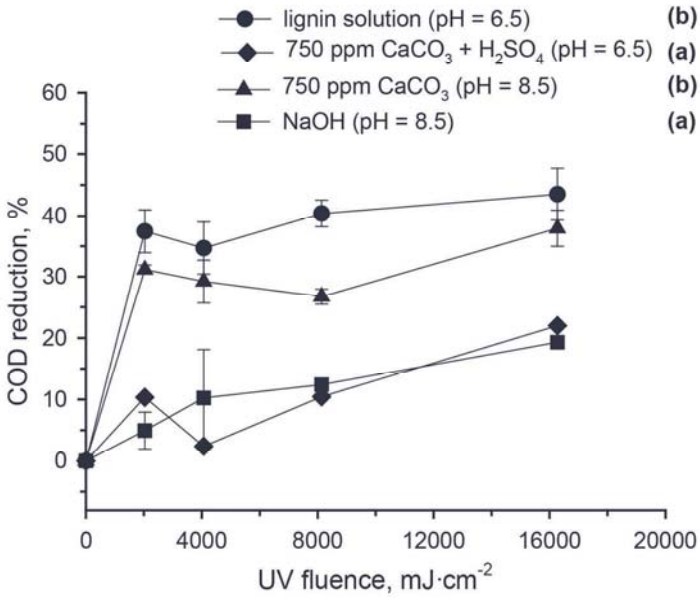

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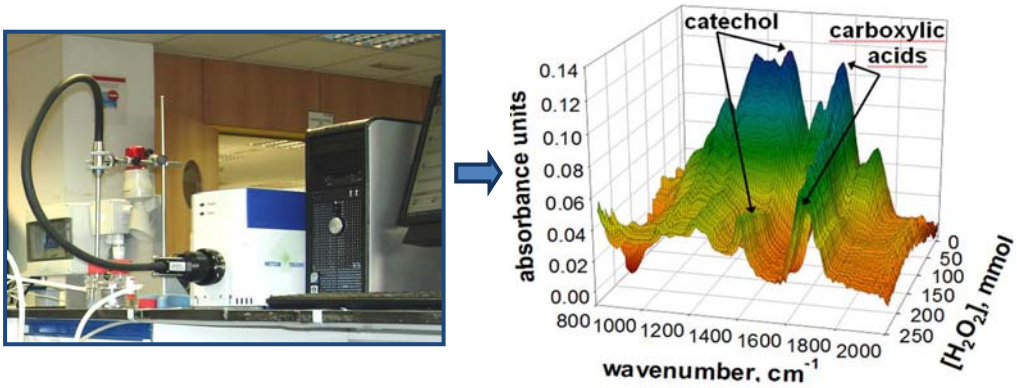

PAPER V

N. Merayo, D. Hermosilla, C. Negro, A. Blanco

On-line FTIR as a novel tool to monitor Fenton process behaviour

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On-line FTIR as a novel tool to monitor Fenton process behavior

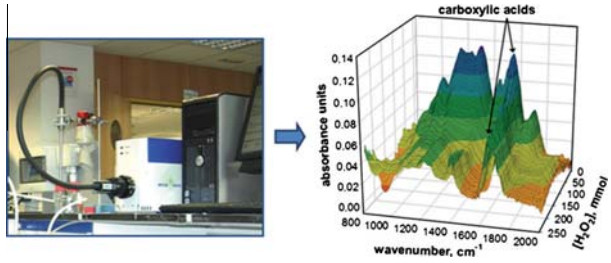
Noemí Merayo, Daphne Hermosilla *, Carlos Negro, Ángeles Blanco

Department of Chemical Engineering, Complutense University of Madrid, Facultad de Ciencias Químicas, Ciudad Universitaria s/n, 28040 Madrid, Spain

HIGHLIGHTS

- On-line FTIR is shown as a suitable alternative for real-time reaction control.
- FTIR was successfully applied to monitor the Fenton oxidation of model compounds.
- FTIR-based real-time control allowed the finest Fenton's process optimization.
- The proposed methodology saved much time for analyses monitoring Fenton processes.

GRAPHICAL ABSTRACT



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ABSTRACT

The efficiency of advanced oxidation processes is usually optimized by measuring the evolution of some water quality parameters sampling aliquots at pre-selected time intervals, such as particular undesired contaminants contents, or the reduction of chemical oxygen demand and total organic carbon. Besides providing good information regarding overall treatment performance and dynamics, this methodology also implies large analytical time consumption, and does not offer the actual full sequence of compounds appearing and disappearing during oxidation. On-line Fourier transform infrared spectroscopy is herein reported as a very useful tool for this purpose. In particular, it was successfully applied to monitoring the Fenton's oxidation of three model compounds (phenol, acetic acid, and oxalic acid) performed in continuous, providing precise control of the effect of reagents over time. Hydroxylation reactions resulted in the formation of hydroquinone and catechol as the main aromatic by-products being generated along the oxidation of phenol by the Fenton process. All phenolic substances (phenol, hydroquinone, benzoquinone, and catechol) were totally removed along the reaction. Carboxylic acids (oxalic and acetic mainly) were significantly present as final by-products of the oxidation process, highlighting their oxyrecalcitrant behavior. On-line FTIR successfully enabled monitoring the Fenton process, and it provided a precise control of the effect of reagents along reaction time. Applications for a future on-line control of Fenton processes in industry may be developed in order to optimize the use of reagents and the potential combination with biological treatment stages; therefore reducing the operational cost of this advanced oxidation treatment.

1. Introduction

Advanced oxidation processes (AOPs) involving the *in situ* generation of highly reactive transitory species (e.g. H_2O_2, $OH^{\cdot}$, O_3, $O_2^{-\cdot}$) are taking advantage when conventional wastewater treatment techniques become insufficient to treat biorefractory contaminants [1–5]. Particularly, the method described by Fenton [6] is one of the most frequently used because it is generally more efficient, and implies a significant lower economical cost than other AOPs [2,5,7,8].

The Fenton process is based on the electron transfer between hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}), which acts as a homogenous catalyst, generating hydroxyl radicals ($OH^{\cdot}$) that can degrade organic compounds [9]. These highly reactive radicals initiate the oxidative destruction of organic substances (RH) present

* Corresponding author. Tel.: +34 91 394 4645; fax: +34 91 394 4243.
E-mail address: dhermosilla@quim.ucm.es (D. Hermosilla).

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in wastewater by hydroxyl radical addition or hydrogen atom abstraction reactions [5]. Organic free radicals ($R^{\cdot}$) are formed as transient intermediates that are further oxidized by hydroxyl radical, hydrogen peroxide, oxygen, ferric iron, and other oxidative intermediates; finally yielding stable oxidized products [5].

The optimization and process control of Fenton treatment and other AOPs has usually been undertaken by measuring certain water quality parameters (e.g. undesired contaminants contents, chemical oxygen demand, and/or total organic carbon removal) at certain time intervals. In addition, several techniques have widely been applied to characterize the sequence of organic compounds that are produced during the oxidative treatment using this discrete sampling protocol, such as high-performance liquid chromatography (HPLC) [10–12], gas chromatography–mass spectrometry (GC–MS) [13,14], Fourier transform infrared spectroscopy (FTIR) [15,16], or different combinations of them, or with other analytic techniques (e.g. ultraviolet–visible spectrophotometry (UV–Vis), liquid chromatography–mass spectrometry (LC–MS), ion chromatography (IC), etc.) [17–21].

Particularly, FTIR has been previously applied to analyze the surface of catalysts and adsorbed substances along diverse AOPs treatments [22–25]. Gas samples have also been analyzed by FTIR to measure the generation of carbon dioxide (assimilable as mineralized carbon) in outlet gaseous streams of ozonation processes, which served as an indirect control parameter of the treatment [26]. In addition, FTIR has also been applied to control reactions in liquid samples identifying the compounds that are appearing and disappearing in the solution at preset time intervals [15,16]. All these methods enabling an indirect discrete control of the reaction involve great analytical time investment, and do not provide a full continuous characterization of the sequence of compounds that are produced in, or removed from the solution along the process. Furthermore, no reference for its on-line application has been reported to date.

On the other hand, membrane-introduction mass spectrometry (MIMS) has actually been applied to perform on-line measurements along photocatalytic processes [27]. Nevertheless, despite this methodology has been reported useful for monitoring these processes on-line, just volatile organic pollutants that are present in water can be effectively analyzed; whereas other highly polar substances could not be detected properly, such as some compounds that have been previously reported to be typically generated along the oxidation process of phenol [27].

Moreover, the current tendency of improving the combination of AOPs with biological technologies [28,29] would surely welcome the application of advanced analytical methods to optimize the efficiency of every treatment step considering the predominant bio- or oxi-degradable nature of by-products. Therefore, the main objective of this essay was developing a suitable methodology of on-line monitoring the evolution of the Fenton treatment of model organic compounds based on FTIR; which may ultimately allow the addition of reagents to be optimized, a further identification of the involved reactions, and the qualitative and quantitative determination of the by-products that are generated along the process.

2. Materials and methods

2.1. Material and analytical methods

All used chemicals were of analytical grade and supplied by PANREAC S.A. (Barcelona, Spain) and Sigma–Aldrich (Highland, USA). Solutions were prepared in ultrapure water and kept in dark until use. 0.1 N H_2SO_4 and 0.1 N NaOH were used to adjust the pH value of the solution along the process.

The concentration of each tested organic compound (16 mmol of phenol, 14 mmol of oxalic acid, and 12 mmol of acetic acid in a total volume of 100 mL) was considered in order to achieve a good monitoring resolution of the process in the ReactIR iC10 device. Phenol was chosen as a model compound to perform this essay because its degradation behavior by several AOPs (Fenton process included) has widely been described previously [30–34], so it would perfectly serve to evaluate the proposed methodology. In addition, oxalic and acetic acids were also chosen due to its oxy-recalcitrant nature [32].

All analyses were made according to the standard methods for the examination of water and wastewaters [35]. Chemical oxygen demand (COD) was measured by the colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermos Scientific AQA 091801, Waltham, USA); and hydrogen peroxide concentration was analyzed using the titanium–sulphate spectrophotometric method [36]. As residual hydrogen peroxide in the solution interferes with COD analysis, this interference was corrected fitting the relationship between COD and hydrogen peroxide content to a second order polynomial equation ($DQO(H_2O_2) = -0.000020\cdot[H_2O_2]^2 + 0.393239\cdot[H_2O_2]$; $R^2 = 99.92\%$; $p = 0.0001$) [37].

Total organic carbon (TOC) was measured by the combustion-infrared method using a TOC/TN analyzer multi N/C® 3100 (Analytik Jena AG, Jena, Germany) with catalytic oxidation on cerium oxide at 850 °C. The integration of the information provided by the evolution of both COD and TOC along the oxidation treatment was assessed by calculating the mean oxidation number of organic carbon ($MOC = 4\cdot[1 - (COD/TOC)]$, considering both COD and TOC in molar units) [32].

Phenol and reaction intermediates were complementary measured by High Pressure Liquid Chromatography (Model L920, Varian, CA, USA) with diode array (PDA) detection. Acetonitrile–water (15%:85%), and (50%:50%) were used as the eluent for aromatics and carboxylic acids, respectively. Sample injections of 20 μL were separated on a C-18 column (Vidac 250 mm × 4.6 mm ID × 5 μm) at 30 °C. The target compounds were measured at the following wavelengths: hydroquinone (290 nm), benzoquinone (245 nm), catechol (280 nm), phenol (270 nm), acetic acid and oxalic acid (200 nm).

2.2. FTIR analytical device

ReactIR iC10 (Mettler-Toledo, Columbia, USA) is a real-time *in situ* reaction monitoring system, based on FTIR spectrometry, that is able to provide all the organic chemical species that are present in the solution as the reaction is being performed . The FTIR spectrometer uses a mercury–cadmium telluride (MCT) detector that is cooled by liquid nitrogen; and measurements are optically taken using a diamond-tipped probe with a 1 m long fibre-optic conduit. This system was purged using instrumental-grade air; therefore preventing water vapour from collecting inside the optics, which may obscure spectral data otherwise.

Data acquisition was performed from 2000 to 650 cm^{-1} with an 8 cm^{-1} nominal resolution. 256 scans were co-added for each spectrum. A background of pure water was carried out using the same resolution and scanning conditions of the trials before each spectral record. These water spectra were subtracted from each corresponding resulting on-line spectra.

Real-time component analyses were performed using ConcIRT software (Mettler-Toledo, Columbia, USA), which applies the curve-resolution mathematical algorithm for grouping wavenumber values that change absorbance intensity in the same way. This software calculates the associated component spectrum and the relative concentration profile in terms of absorbance units for each group; and it re-analyzes and updates all spectra and concentra-

tion profiles as each new reaction spectrum is acquired. In short, calculation results evolve as the reaction proceeds, and every organic component (reagent, intermediate or product) that is present in the solution is detected in real-time; and its relative concentration profile is therefore provided.

2.3. Experimental procedure

Experiments were performed in the dark inside a 500 mL glass reactor where 100 mL of the solution were continuously stirred (300 rpm) with a magnetic device at room temperature (≈20–25 °C). All experiments were repeated three times. pH = 2.8 (±0.2) was kept constant along the process. pH adjustment was required until this 2.8 value was monitored stable and no further regulation was necessary. The concentrations of reagents were chosen to meet the following ratios: $[H_2O_2]/COD_0 = 2.15$, and $[H_2O_2]/[Fe^{2+}] = 37.5$; as these reaction conditions have previously been reported to produce optimal Fenton treatment results for the target substances [30,32].

The required amount of ferrous sulphate was added in batch mode after the initial pH value was adjusted. Hydrogen peroxide was thereafter added in continuous mode, so all the designed dosage of this reagent was supplied after 120 min of reaction. In fact, the continuous addition of H_2O_2 has already been reported to provide better results than batch mode in previous trials of this process [31,37]. In addition, it also allows a better understanding of the process enabling the use of the added quantity of H_2O_2 (milimol), rather than reaction time, as an indicator of the progress and evolution of oxidation.

Additional trials were performed in equal conditions in which aliquots of the solution were withdrawn with a syringe in order to monitor the overall progress of the reaction in terms of COD removal and H_2O_2 consumption. This way, volume changes did not alter FTIR-monitoring runs. These samples were neutralized to pH = 9.0 with 40% NaOH, mixed, and centrifuged for 15 min at 2000 rpm, before collecting the supernatant where COD and $[H_2O_2]$ were determined.

The ReactIR iC10 probe placed inside the reactor monitored the whole reaction progress in real time. In order to properly read and calibrate spectral results, the characteristic bands of the main compounds that were expected to be produced during the Fenton treatment of the target substances were crosschecked using the available information found in bibliography (Table A.1), and our own collected spectra from conveniently prepared control solutions containing just one of these compounds (Figs. A.1 and A.2), which have been included in Appendix A. Despite the similarity of some by-products of the reaction, the full interpretation of the generated complex spectra recorded during the trials was successfully achieved thanks to the mathematical algorithms provided by ConcIRT software.

3. Results and discussion

3.1. Degradation of phenol by the Fenton process

All three repetitions of every performed experiment reproduced the same results, and there were not found meaningful differences among them.

Spectra within the region of 650–2000 cm^{-1} continuously increased during H_2O_2 addition until 60 mmol of H_2O_2 were added in total, when the highest overall absorbance was reached. Subsequently thereafter, the overall spectra began to decrease and all peaks progressively became smoother (Fig. 1).

After the first addition of H_2O_2, the color of the solution instantaneously changed from colorless to dark brown (almost black) due to the oxidation of ferrous to ferric ion, and the generation of quinones (i.e. hydroquinone and benzoquinone, Fig. 2) in redox equilibrium [31,33], which are more toxic than phenol itself [31]. This dark color gradually lost its intensity thereafter, and a pale orange color remained after adding a total 160 mmol of H_2O_2 (when its ratio to the initial amount of phenol was 10) because quinones have already been degraded; as well as due to the remaining presence of several by-products of acid formation stages (oxalic acid, mainly) [32,33] that are able to reduce ferric back to ferrous iron [38]. Similar color changes have been addressed before [33,39]. Furthermore, HPLC analyses confirmed these FTIR results.

The evolution of MOC along treatment (Fig. 2) also supports this affirmation linearly changing from an initial value of −0.67, which is characteristic for phenol, to ≈3, which has previously been addressed to a mix of carboxylic acids where oxalic (MOC = 3) predominates [32]; and then it remained constant thereafter.

The concentration profile of phenolic compounds resulted mainly integrated by phenol itself and some products that are generated by its hydroxylation, namely hydroquinone, benzoquinone

Table A.1
Characteristic wavenumber peaks of relevant organic compounds that are produced during the Fenton oxidation of phenol, oxalic acid and acetic acid.

Phenol	Hydroquinone	Resorcinol	Catechol	Benzoquinone	Oxalic acid	Acetic acid	Formic acid	$FeSO_4{\cdot}7H_2O$	References
Wavenumber (cm^{-1})									
					1738				[47]
						1707			[16]
				1638					[48]
					1621				[47]
1595		1604	1604	1599					[16,22,25,49–51]
					1574 (anion)				[47]
1501									[16,22,25]
1475	1472								[16,22,25]
						1410			[16]
		1381							[49]
			1379						[49,50]
1372									[16,22,25]
	1367								[16]
					1310 (anion)				[47]
						1292			[16]
1235					1232				[16,22,25,47]
					1226				[35]
			1200						[16,49,50]
								1089	[51–53]
809									[16,22,25]
752									[16,22,25]

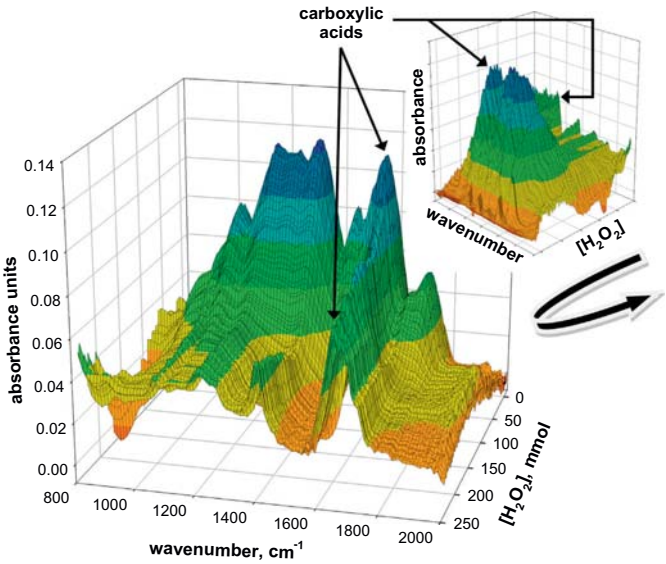

Fig. 1. Evolution of FTIR-spectra along a continuous hydrogen peroxide addition in the Fenton oxidation of phenol. The presence evolution of carboxylic acids is highlighted, and a turned around graph is also shown in small detail. (Reaction conditions: room temperature (≈20–25 °C); pH = 2.8 ± 0.2; 16 mmol phenol; $[H_2O_2]/COD_0$ = 2.15; $[H_2O_2]/[Fe^{2+}]$ = 37.5).

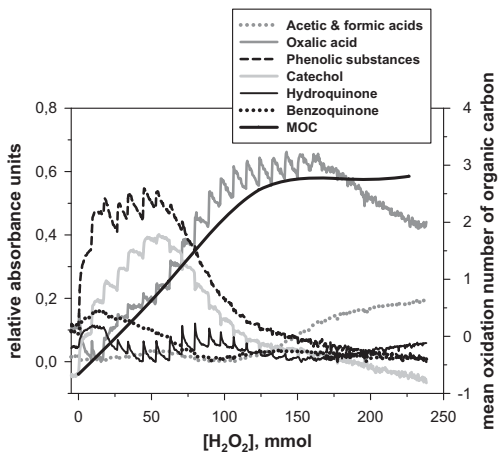

Fig. 2. Absorbance profiles for main by-products, and evolution of the MOC along a continuous hydrogen peroxide addition in the Fenton oxidation of phenol (Reaction conditions: room temperature (≈20–25 °C); pH = 2.8 ± 0.2; 16 mmol phenol; $[H_2O_2]/COD_0$ = 2.15; $[H_2O_2]/[Fe^{2+}]$ = 37.5).

[31,33,40] and catechol (Fig. 2). On the other hand, resorcinol was not actually found along the Fenton oxidation of phenol. In fact, its formation would rather be implausible based upon the substitution rules of organic chemistry [33]; and it may anyhow occur in an about one thousand times lower frequency than the generation of catechol and hydroquinone [34].

The absorbance concentration profile of phenolic compounds logically increased as phenol was added to the solution; and it also grew again after the addition of H_2O_2 because other phenolic intermediate compounds of the reaction were newly formed (Fig. 2). During the reaction, this phenolic mix totally disappeared when the concentration ratio between the added H_2O_2 and the initially supplied amount of phenol was close to 8, coinciding with previously reported results on the Fenton oxidation of phenol and nitrophenol, when a MOC value characteristic of the predominant presence of carboxylic acids (≈2.5–3) was kept more or less constant as the reaction progresses (Fig. 2) [32].

Achieving the total degradation of hydroquinone is of environmental concern due to its high toxicity, which is several orders of magnitude higher than the attributed to phenol itself [29]. On the other hand, catechol also resulted totally removed at the end of the reaction, as it has been clearly addressed by HPLC measurements. Nevertheless, catechol is highly biodegradable [41,42]; thus, it might be further treated by biological technologies, which are, in general, cheaper treatments than AOPs.

Furthermore, previous results reporting a significant much higher production of catechol than hydroquinone along the process were confirmed [33,34], as it results from comparing the concentration profiles of both compounds in Fig. 2. In fact, the production of catechol resulted a 100% higher than the measured for quinones by HPLC. In short, catechol and hydroquinone were initially formed as phenol disappeared; and then, they began to be gradually degraded competing with their own further formation as phenol was still being oxidized.

In addition, phenol decreased its concentration in the solution faster than the other newly generated phenolic intermediates (hydroquinone, benzoquinone, and catechol) of the reaction (comparing Figs. 2 and 3); which is also in accordance to previous scientific reports [32–34]. Only a 4% of phenol remained after adding a ratio of H_2O_2 to phenol of 3.9; results that were further confirmed by HPLC analyses.

At this point, the removal of COD was higher than 50%, and it did not show further lineal progress (Fig. 3). Finally, phenol resulted totally degraded when the aggregated concentration of H_2O_2 reached 5.6 times the initial amount of added phenol, and the reduction of the COD was close to a 75%; showing a further asymptotic evolution because of the growing presence of carboxylic acids, which are more difficult to oxidize. Hereafter, the mix

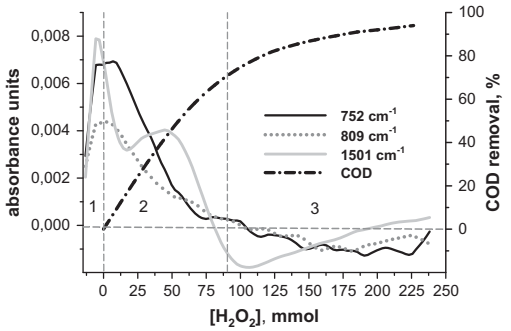

Fig. 3. Smooth absorbance concentration profiles of phenol, and evolution of the removal of the COD along the Fenton oxidation of phenol considering all its three typical detection wavenumbers (752, 809, and 1501 cm^{-1}). Note: 1 = addition of reagents; 2 = progressive removal of phenol; 3 = after the total removal of phenol.

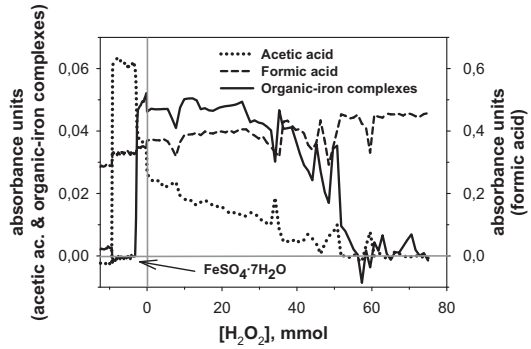

Fig. 4. Concentration profiles of acetic acid, formic acid and organic-iron complexes during the degradation of acetic acid by Fenton's reagent. (Reaction conditions: 12 mmol acetic acid, pH = 2.8 ± 0.2, $[H_2O_2]/[Fe^{2+}]$ = 37.5).

of phenolic compounds remaining in the solution was mainly made up by hydroquinone and catechol (Fig. 2), which absorbance concentration profile quickly decreased until the ratio between the total added H_2O_2 and the initial amount of phenol was close to 6.5. Then, its abatement thereafter progressed smooth, and its total degradation was finally achieved when this ratio arrived to about 8, as confirmed by HPLC determinations.

Some carboxylic acids remained in the solution at the end of the process as the main persistent by-products of the oxidation treatment of phenol (Fig. 1); although they are also considered highly biodegradable and might be further treated by biological processes [41,42]. Oxalic, acetic, and formic acids were identified as the resultant products of an acid formation stage within the process. Its presence and persistence was also confirmed by HPLC measurement, and MOC and COD behavior assessment (Figs. 2 and 3), as just stated before. That is, its presence resulted constant after the ratio of total added H_2O_2 to the initial amount of phenol reached a value close to 8, which was accurately measured by HPLC; and also confirmed by a nonfurther change of MOC from characteristic values previously addressed for carboxylic acids mix [32], although COD was still slightly being removed (Figs. 2 and 3).

In short, carboxylic acids were probably formed by ring-opening reactions that take place within degradation stages of some aromatic intermediate products of the reaction [32,33]. Whilst the presence of oxalic acid was detected from almost the beginning of the reaction (Fig. 2), when the ratio of total added $[H_2O_2]$ to the initial concentration of phenol was just 1.8; acetic and formic acids presence was noticed in the solution when this ratio reached 6.25, suggesting that these two carboxylic acids may be generated by the degradation of some other intermediate reaction by-products.

All these carboxylic acids that are inevitably formed during the oxidative degradation of phenol are more or less recalcitrant to its further Fenton advanced oxidation treatment [1,16]; so they will hereafter be considered as oxyrecalcitrant compounds [32]. In fact, this limited capacity to degrade carboxylic acids is one of the main drawbacks for achieving the total mineralization of phenol by Fenton's reagent [32,33]. Therefore, the main objective of AOPs based treatment steps might be defined as controlling the process until a maximum biodegradability threshold is achieved in order to combine this treatment with a cheaper posterior biological stage [43].

In summary, a final 94% reduction of the COD was achieved (Fig. 3), which is even higher than previously reported results [30,32]. The continuous addition of H_2O_2, which has previously been proved to enhance the removal of COD in comparison to batch mode [37], as well as the steady thorough control of the reaction conditions that was performed, have surely served well to achieve this very successful result. The 6% remaining COD was held by the remaining mix of oxyrecalcitrant by-products, oxalic and other carboxylic acids, mainly.

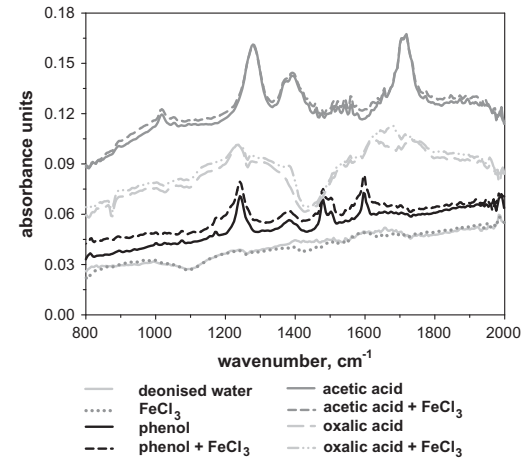

Fig. 5. FTIR spectra resulting for deionised water, phenol, acetic acid, and oxalic acid with and without the presence of ferric chloride trihydrate.

3.2. Fenton treatment of acetic acid

When trying to oxidize acetic acid by Fenton's reagent, the initial addition of $FeSO_4 \cdot 7H_2O$ resulted in a colorless solution because the high production of a complex that is formed between acetic acid and ferrous iron drastically reduced the presence of both compounds in the solution (Fig. 4). As H_2O_2 was thereafter added, the concentration of this complex began to decrease, and the solution turned to an orange-reddish color as ferric ion was generated [38], which further induced the formation of an acetic acid–ferric iron complex. The formation of this complex is stronger than the acetic acid–ferrous iron one [32], but it was not detected by FTIR in the spectral region under study (Fig. 5). Nevertheless, the clearly noticed orange color of the solution, and the very limited figures of COD reduction, clearly suggest the presence of this ferric–acetic acid complex, as it has previously been reported [32].

The reaction may be considered finished when the ratio between the added concentration of H_2O_2 and the initial amount of supplied acetic acid reached 4.8. At this moment, the organic-fer-

rous iron complex disappeared because there was not any available Fe^{2+} to form more $OH^{\cdot}$ that might have further continued the oxidation process, and the acetic acid–ferric iron complex (not visible to FTIR) and formic acid (Fig. 5) remained in the solution as the final result of the attempted degradation of acetic acid by the Fenton's reagent [44,45]. Final COD reduction figures were just about a 9% due to the above mentioned oxyrecalcitrant nature of this type of chemicals. In fact, these poor treatment results fully agree with other previously reported ones [32].

3.3. Fenton oxidation of oxalic acid

A constant weak green–yellow color predominated in the solution along the treatment of oxalic acid by Fenton's reagent; even after H_2O_2 was added. Therefore, ferrous to ferric ion oxidation was occurring at a very low pace; being oxalic acid itself contributing to reduce ferric back to ferrous [38]. This process partially slowed the oxidative process down because some H_2O_2 was being wasted on oxidizing ferrous iron back to ferric one.

In short, Fenton oxidation did not produce any degradation of oxalic acid (Fig. 6). In fact, great Fe^{2+} losses have previously been attributed to the formation of a strong oxalic–ferrous complex, which consequently hinders the oxidation process to progress [32]. Although this oxalic–ferrous complex was not detected by the FTIR probe, probably due to its very close likeness to other oxalic compounds, the oxidation process resulted similarly hindered.

In fact, the absorbance concentration profile of oxalic acid did not show any change after increasing the addition of H_2O_2 (Fig. 6); although it significantly decreased previously, just after adjusting the pH (adding 40% NaOH), because oxalic acid and oxalate anion contents depend on the pH value of the solution [46]. That is, oxalate anion was formed as pH increased, as it is detailed in Fig. 7. Whereas the characteristic wavenumber peaks of oxalic acid (1733 and 1232 cm^{-1}) gradually decreased during the addition of 40% NaOH until its content stabilized at a very constant final value [46]; those typical peaks of oxalic anion (1571 and

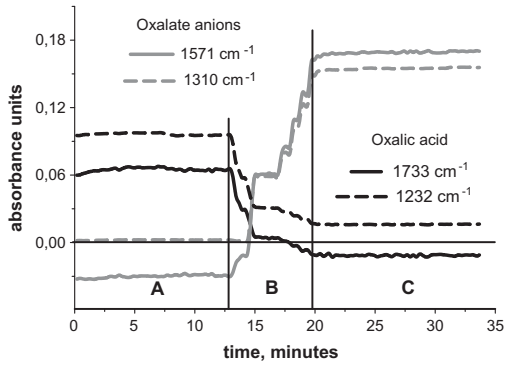

Fig. 7. Absorbance concentration profiles for characteristic wavenumber values of oxalic acid (1733 and 1232 cm^{-1}) and its anion (1571 and 1310 cm^{-1}) considering the following pH turns: (A) natural pH of an oxalic acid solution, (B) 40% NaOH addition to increase pH, and (C) pH values at which oxalic forms are stabilized (>9.0).

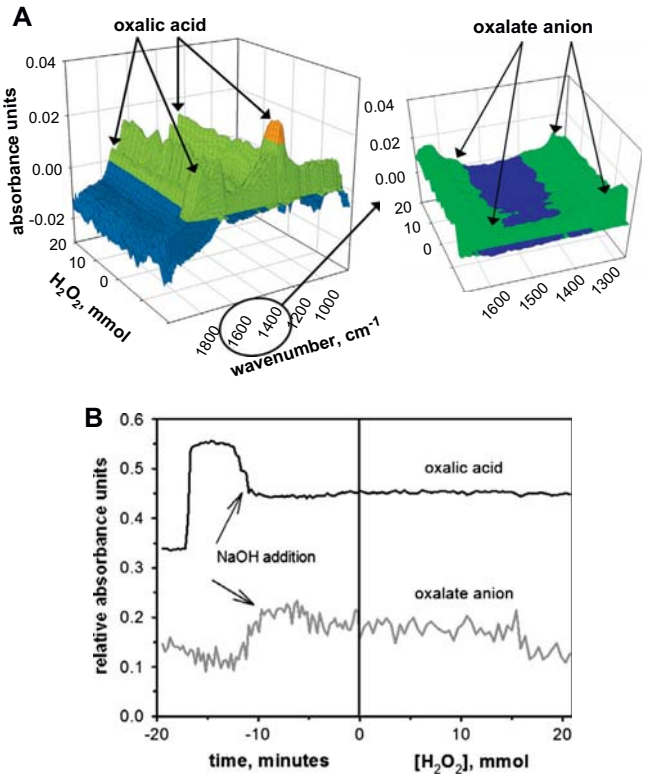

Fig. 6. Evolution of FTIR spectra in the span ranging from 2000 to 800 cm^{-1} (A), and concentration profiles of oxalic acid and oxalate (B) along the Fenton oxidation of oxalic acid. (Reaction conditions: 14 mmol oxalic acid, pH = 2.8 ± 0.2, $[H_2O_2]/[Fe^{2+}]$ = 37.5).

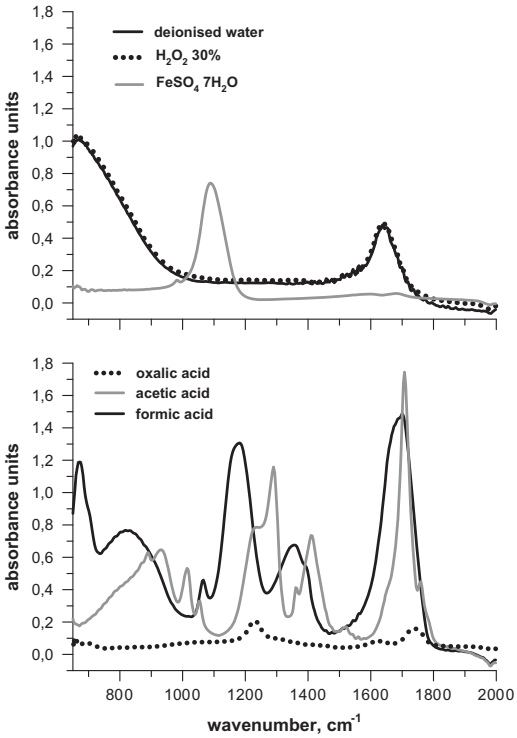

Fig. A.1. FTIR spectra of main inorganic and aliphatic compounds that are used and may be produced in the oxidation of phenol by the Fenton process.

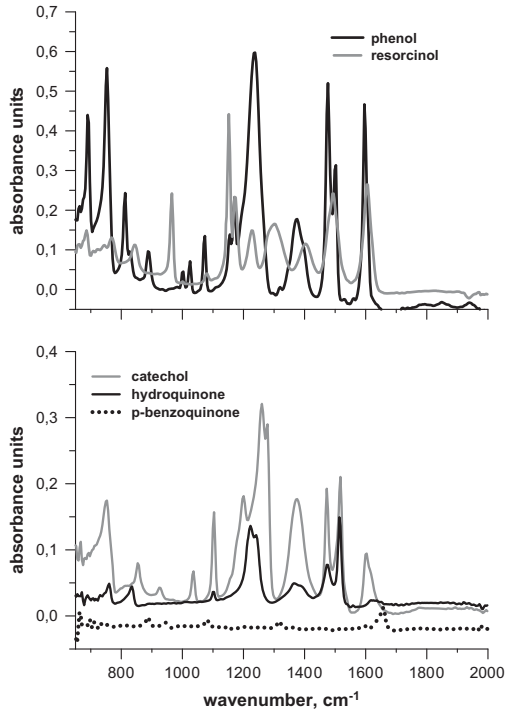

Fig. A.2. FTIR spectra of main aromatic chemicals that may be produced in the oxidation of phenol by the Fenton process.

1310 cm^{-1}) showed up, and correspondingly increased its absorbance record, after NaOH was added, until its content reached a steady state as well [46].

Summing up, the total removal of the COD that was achieved in the treatment of oxalic acid by Fenton's reagent resulted lower than the 7%. This result totally meets previously reported results [31,32], which also suggested that it is the variation of pH, rather than the oxidative treatment itself, which is the responsible of this reduction of the COD. In fact, this slight percentage of COD removal was surely the result of the final precipitation of oxalic acid when pH was turned to 9 adding NaOH at the end of the reaction aiming to remove iron precipitating its hydroxides.

4. Conclusions

The above reported results clearly show that the effectiveness of an oxidation process may successfully be assessed by FTIR, implying a significant reduction of the time devoted for analyses in comparison to other methodologies. In addition, it has been shown that the results obtained by FTIR were in total agreement with those previously reported using chromatographic analyses. That is, aliphatic organic compounds were not easily degraded with this type of treatment, whereas phenol resulted totally removed.

The quality and quantity of reaction intermediates that were produced during the oxidative degradation of phenol were fully assessed, and the mechanisms that were involved were also well observed. Thanks to receiving real-time information, this procedure allowed a precise control of the effects of reagents on the treated substances, which furthermore enabled optimizing the quantities of reagents required in the process. This may further enable the successful optimization of the treatment combination of AOPs with biological technologies, as the reaction moment where oxyrecalcitrant (but biodegradable) substances were mainly present in the solution was clearly identified.

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Appendix A

Spectral characteristics of the chemical species produced along the Fenton oxidation treatment of phenol.

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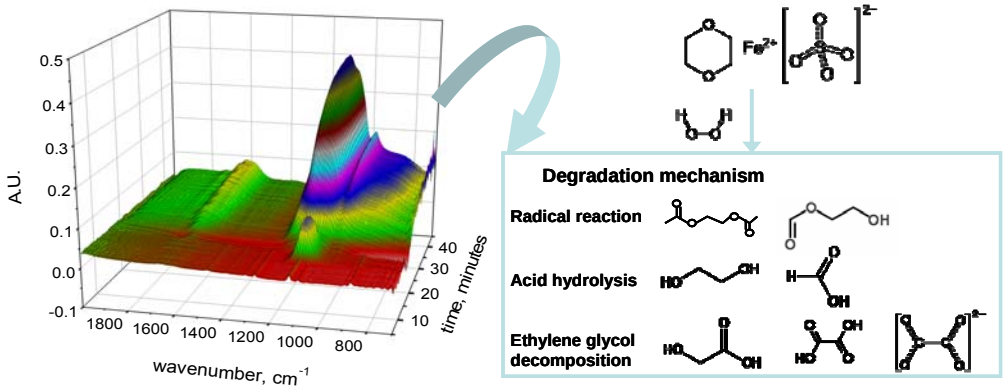

PAPER VI

N. Merayo, D. Hermosilla, L. Cortijo, A. Blanco

Optimization of Fenton treatment of 1,4-dioxane applying on-line control of the reaction

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Optimization of the Fenton treatment of 1,4-dioxane and on-line FTIR monitoring of the reaction

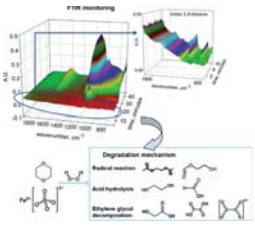
Noemí Merayo, Daphne Hermosilla*, Luis Cortijo, Ángeles Blanco

Department of Chemical Engineering, Complutense University of Madrid, Facultad de Ciencias Químicas, Ciudad Universitaria s/n, 28040 Madrid, Spain

HIGHLIGHTS

- 1,4-Dioxane can be totally removed applying an optimized Fenton process.
- FTIR-based monitoring of compounds presence along treatment was accomplished.
- A degradation route is proposed for the Fenton treatment of 1,4-dioxane.

GRAPHICAL ABSTRACT



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ABSTRACT

1,4-Dioxane is a non-biodegradable, toxic, hazardous, and priority pollutant widely used in the chemical industry as a solvent; as well as it is a resulting by-product of many industrial processes. The optimization of the Fenton treatment of 1,4-dioxane, and the on-line FTIR monitoring of its degradation route, including the assessment of the enhancement of the biodegradability of the solution along treatment are herein addressed. Besides the full removal of 1,4-dioxane, an 80% reduction of the chemical oxygen demand (COD) was achieved at the best tested treatment conditions. Whether the used concentration of H_2O_2 was expectedly addressed as the reaction factor most influencing the achieved COD removal at the end of the process; the performance of the treatment under acid pH conditions showed to have just a slight influence, thus supporting this process may suitably be performed at neutral pH value. On-line FTIR monitoring of the process novelly provided the degradation route of 1,4-dioxane along its oxidation treatment, as well as a comprehensive optimization of the Fenton process based on the increase of the biodegradability of the solution and the reduction of the consumption of reagents.

1. Introduction

1,4-Dioxane is an organic compound used as solvent in many industrial processes, as well as it is generated as a by-product in several industrial chemical reactions [1]. The main environmental concern regarding the potential release of this compound to the environment has recently increased due to its major negative effects on health. Correspondingly, 1,4-dioxane is classified as a priority pollutant by the US EPA [2]. Furthermore, it is a bio-recalcitrant and persistent organic molecule that cannot be treated by conventional bio-treatment technologies [1,3]. In fact, physical treatments, such as adsorption on activated carbon or air striping, have not been successful removing dioxane from water because of this inherent high aqueous solubility and its low vapor pressure [3,4]. Moreover, it has been addressed that the chemical oxidation of 1,4-dioxane by chlorine could lead to the formation of even more toxic compounds [1]. In conclusion, traditional treatments have not been shown as effective degrading this substance. Only distillation technology has efficiently been proved to separate 1,4-dioxane from the solution due to its high volatility; but

* Corresponding author. Tel.: +34 91 394 4645/+34 91 394 4245; fax: +34 91 394 4243.
E-mail addresses: nmerayoc@quim.ucm.es (N. Merayo), dhermosilla@quim.ucm.es, dahermosilla@yahoo.es (D. Hermosilla), lcortijo@quim.ucm.es (L. Cortijo), ablanco@quim.ucm.es (Á. Blanco).

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its use has a very high associated cost, particularly at very low concentration levels [1,3,4].

Advanced oxidation processes (AOPs) may represent a feasible treatment alternative for 1,4-dioxane [4] because they can be applied at a lower economical cost just transforming this persistent compound into simpler more biodegradable compounds that might be further degraded by traditional biological treatment [5]. Particularly, Fenton method is one of the most commonly used AOPs. It is based on the electron transfer between hydrogen peroxide and ferrous ion, which acts as a homogenous catalyst, yielding hydroxyl radicals (OH•) that are able to degrade a wide range of organic compounds [6]. In general, the Fenton process is usually very efficient, and it even implies a lower economical cost than the application of others AOPs [7]. Regardless a high chemical oxygen demand (COD) removal efficiency could be achieved and a relative overall environmental friendliness, a Fenton treatment of wastewater is limited by the final production of iron sludge, which requires ultimate disposal [8], and the optimal pH range of application, which is usually set at acid values (pH≈3) [9,10].

There are very few limited studies considering the treatment of 1,4-dioxane by Fenton's reagent [1,3,11]. Although all these essays have assessed the improved elimination of 1,4-dioxane and COD from wastewater, an increased biodegradability of the final solution, and the reduced consumption of reagents; a comprehensive process optimization has not been addressed yet. In fact, the identification of which by-products are formed along the degradation of 1,4-dioxane by Fenton has not been addressed to date. Some authors have previously reported the removal of 1,4-dioxane and other by-products that are formed along its treatment, but the production of other chemical species along the reaction has not really been assessed in full yet [1,11,12]. Only Stefan and Bolton [13] have previously proposed a degradation mechanism for 1,4-dioxane treating this chemical by UV/H_2O_2 and taking periodical samples that were analyzed by gas chromatography (GC), solid phase microextraction (SPME), gas chromatography/mass spectrometry (GC/MS), ion chromatography (IC), and high-performance liquid chromatography (HPLC), in order to identify intermediate chemical species and by-products. The advantage of monitoring similar processes using Fourier transform infrared spectroscopy (FTIR) has previously been addressed identifying the compounds that are appearing and disappearing in the solution along the reaction sampling aliquots at preselected time intervals [14,15].

Therefore, the main objectives of this research are: (1) optimizing conventional Fenton method as a promising alternative for the treatment of 1,4-dioxane; and (2) developing an FTIR-based methodology enabling the on-line control of the use of reagents, and the production of intermediates and by-product along the degradation of 1,4-dioxane.

2. Material and methods

2.1. Materials and analytical methods

All used chemicals were of analytical grade and supplied by PANREAC S.A. (Barcelona, Spain) or Sigma-Aldrich (Highland, USA). The solutions were prepared in deionized water and kept in the dark until use. All the analyses were made according to the standard methods for the examination of water and wastewaters [16]. COD was measured by the colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermo Scientific AQA 091801, Waltham, USA). Hydrogen peroxide concentration was analyzed by the titanium sulphate spectrophotometric method [17].

In order to confirm FTIR results, 1,4-dioxane and ethylene glycol were identified and quantified along the reaction by gas-liquid chromatography (GLC) using a 7980A instrument (Agilent Technologies Inc., Palo Alto, CA) equipped with a flame ionization detector. Injector and detector were respectively set up at 310 and 280 °C. Samples (2 μL) were injected using the *pulsed-split* mode (*split* ratio 5:1) and analyzed in a TRB-FFAP (Teknokroma, Sant Cugat del Vallès, Spain) fused silica column (30 m × 0.25 mm internal diameter × 0.25 μm film thickness), with He (43 psi) as carrier gas, and the following temperature program: 80 °C to 240 °C at a 15 °C min^{-1} ramp rate after a 9 min initial hold. Peaks were identified on the basis of sample coincidence to relative retention times of commercial standards. Quantification was performed according to peak areas that were corrected by response factors that were calculated for each compound using 1-butanol (250 mg L^{-1}) as internal standard, and *GC-ChemStation Rev.B.04.02 (96)* software from Agilent.

Formic, oxalic, acetic, glycolic, and methoxyacetic acids were also complementarily identified and quantified by ion chromatography (IC) using a Dionex DX-500 device (Thermo Scientific, Sunnyvale, CA) equipped with a conductivity detector. A 40 to 60 mM NaOH gradient was used as the eluent for measurement keeping the flow at 1.5 L min^{-1}. The injection loop was 75 μL. An AS11HC Ion Pac ionic resin column was used aided with a previous Anion Trap Column (ATC3) and a AG11-HC guard column. Peaks were identified and quantified on the basis of sample coincidence to relative retention times and standard concentrations of commercial standards.

2.2. FTIR analytical equipment

Mettler-Toledo ReactIR iC10 (Columbia, USA) is a Fourier transform infrared (FTIR) spectrometer that measures chemical species as they react over a period of time. It uses a Mercury Cadmium Telluride (MCT) detector that is cooled by liquid nitrogen. Measurements are optically taken using a diamond tipped probe with a 1 m fiber optic conduit. The system should be purged (using instrument grade air, nitrogen or other suitable inert gas) in order to prevent water vapour from collecting inside the optics, which might otherwise obscure spectral data.

Data acquisition in the absorbance scale was taken from 2000 to 750 cm^{-1} with an 8 cm^{-1} nominal resolution; and 256 scans were co-added for each spectrum. A background on pure water was carried out just before performing each spectral record under the same resolution and scanning conditions that were used for the trials. Real-time component analyses were run using ConcIRT software (Mettler-Toledo, Columbia, USA), which calculates associated component spectra, and relative concentration profiles.

2.3. Experimental procedure

Experiments were performed in a 500 mL glass reactor placed on a magnetic mixing device. Temperature was adjusted to the desired value (25 °C) using a water heater and circulator. pH was monitored along the process, and adjusted to the desired value (±0.1) using 1 mol L^{-1} sodium hydroxide, or 1 mol L^{-1} sulphuric acid, as required. Considering 1,4-dioxane is degraded to ethylene glycol at a very slow rate at acid pH values, whereas it is ionized and keeps a stable structure under basic ones, pH adjustment was carried out after adding dioxane (247.8 mg L^{-1}; initial COD = 450 mgO_2 L^{-1}) when performing trials under acid conditions, and before its incorporation to the solution otherwise. After temperature and initial pH adjustment, ferrous sulphate was added to the solution at the ferrous ion concentration specified in the experimental design described next to optimize treatment results. Hydrogen peroxide (30% w/v) was then added in batch mode until the designed concentration was also reached. Treatments were run until all the added H_2O_2 was totally consumed, so maximum COD removal was achieved for a set of reaction variables values.

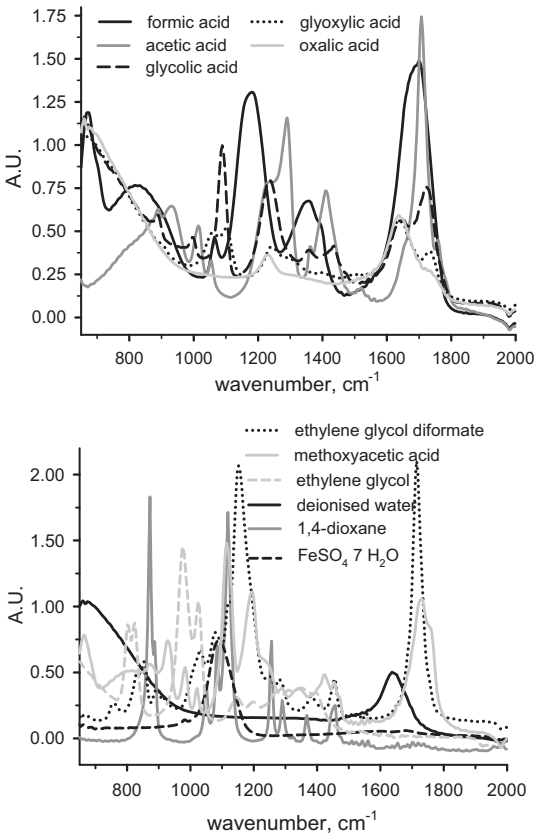


Fig. 1. Reference spectra for the main chemicals that are expected to be found along the Fenton oxidation treatment of 1,4-dioxane.

Aliquots of the treated solution were periodically sampled with a syringe along the trials. These samples were adjusted to pH≈9.0 adding 40% sodium hydroxide (NaOH), and then centrifuged during 15 min at 2000 rpm. COD and H_2O_2 concentrations were measured in the collected supernatant. H_2O_2 concentration values were used to correct COD values according to Hermosilla et al. [18].

Initial reaction conditions and concentrations of reagents chosen to perform on-line FTIR control experiments were determined after optimizing the Fenton treatment of 1,4-dioxane. In general, the experimental procedure used for FTIR trials was the same, despite the concentration of 1,4-dioxane was 0.07 mol L^{-1}, and the addition of hydrogen peroxide was carried out in continuous mode (8.8 mmol H_2O_2 min^{-1} to a total 100 mL of reaction solution) because it allows to understand better the reaction process; besides it has previously shown better results than batch mode in this particular process [18,19].

The main compounds that actual scientific literature proposes to be considered in the degradation route of 1,4-dioxane by oxidation are: ethylene glycol diformate, glycolic acid, glyoxylic acid, methoxiacetic acid, formic acid, acetic acid and oxalic acid [1,3,11,13,20]. Their reference spectra were first experimentally collected by FTIR (Fig. 1). Despite the likeness of these compounds, the proper interpretation of mixture spectra (recorded during Fenton processes) have been successfully carried out with the help of the mathematical algorithms integrated in ConcIRT software, and comparing spectra of pure solutions with those obtained along the process. Water spectra were subtracted from the obtained on-line spectra in all experimental runs.

2.4. Experimental design

Response surface methodology (RSM) was used to optimize the Fenton treatment of 1,4-dioxane statistically assessing the significance of the effects of the considered individual factors, and the interactions between them, that influence the process [21,22]. In addition, Pareto charting was used to highlight the most important factors that influenced the treatment efficiency. In short, this methodology allows determining optimum operation conditions for the system, as well as the region in which the operating specifications are satisfied [22]. Experimental design, regressions, response surfaces, and Pareto charts, were run by Systat 13 software (SYSTAT Software Inc., Chicago, USA). pH, temperature, the concentrations of reagents, and reaction time, are the main factors that may influence the Fenton treatment of an organic compound. Among them, temperature has previously been reported not to affect much between 25 to 45 °C, and reaction time is really dependent on the concentrations of reagents [18]. Therefore, experiments were designed to optimize pH, hydrogen peroxide and ferrous ion concentrations. Based upon previously reported results for optimizing Fenton treatment of organics [23], RSM was actually performed considering pH values of 2.8, 5.0 and 7.2; and H_2O_2 concentration dependent ratios of $[H_2O_2]_0/COD_0$ = 1.063, 2.125 and 4.250; and $[H_2O_2]_0/[Fe^{2+}]_0$ molar ratios of 1.0, 5.0 and 10.0.

In short, RSM regression analysis was performed according to a full factorial design (N = 27) using the following quadratic model:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} X_i X_j$$

where Y (COD removal) is the process response dependent variable; X_i are the considered independent variables ($X_1 = [H_2O_2]_0/COD_0$; $X_2 = [H_2O_2]_0/[Fe^{2+}]_0$; X_3 = pH); and b_i, b_{ii} and b_{ij} are the corresponding regression coefficients.

3. Results and discussion

3.1. Optimization of the conventional Fenton treatment of 1,4-dioxane

pH is one of the most important factors influencing the final result of a Fenton process because it mainly controls the speciation of iron and the stability of hydrogen peroxide [24,25].

In short, iron precipitation as $Fe(OH)_3$ is avoided under acid conditions because the solubility of iron increases [26] and, as a consequence, the efficiency of the process also increases. In addition, hydrogen peroxide decomposition is also impeded under acid environments, favoring its stabilization [27]; as well as the scavenger function of inorganic carbon is also prevented because it should mainly have already been removed. Nonetheless, further significance may be found in the case of the Fenton treatment of 1,4-dioxane because of the structural changes this compound shows in relation to the pH value of the solution.

The resulting estimations of the regression coefficients of the quadratic model used to optimize the Fenton treatment of 1,4-dioxane by RSM (Fig. 2) are shown in Table 1. Whether a positive value of one of these coefficients indicates a positive relation of the associated factor to COD reduction; negative coefficients mean a lower COD removal would be achieved at a higher value the related factor. In particular, the negative coefficient related to the pH factor means that higher COD reductions were achieved working at lower pH values (Fig. 2); as well as higher doses of H_2O_2 (a higher

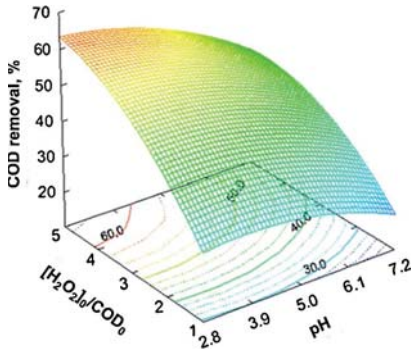


Fig. 2. Response surface and contour plot for the reduction of the COD resulting in the Fenton treatment of 1,4-dioxane (247.8 mg L^{-1}) being performed at different pH and reagents concentrations values (T = 25 °C).

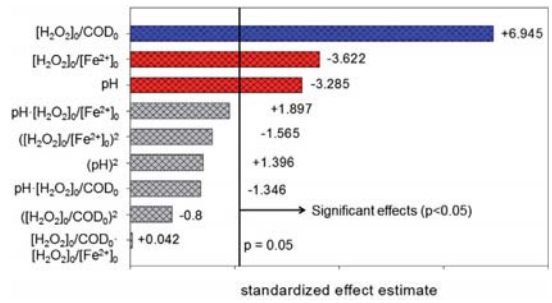


Fig. 3. Pareto chart including the degree of influence of each considered factor in the Fenton treatment of 1,4-dioxane.

$[H_2O_2]_0/COD_0$ ratio, actually) increased the difference between the reduction of the COD that was achieved working at those designed lower and higher pH values. In fact, the effect of pH was slight at the designed lower dose value of H_2O_2 (less than 10%).

The optimum pH value for performing the Fenton treatment of 1,4-dioxane resulted 2.8, as it has previously been also reported, although the effect of pH was not as relevant as it has been addressed before [18,28]. The highest influence of pH was exerted at a ratio of $[H_2O_2]_0/COD_0$ = 4.250, obtaining a good COD removal result (≈55%) when the process was performed at pH = 7.2 if it is compared to the optimized result at pH = 2.8 (COD removal ≈65%; Fig. 2). This shorter difference in the efficiency of the process being performed at both pH values was probably the result of the structural changes that are promoted in the molecule of 1,4-dioxane when the pH value changes from acid to basic. In fact, the ionization of 1,4-dioxane under basic reaction conditions favors its reaction with hydroxyl radicals. As a result, the use of chemicals for controlling the pH may be partially counterbalanced as the main drawback for the implementation of Fenton process at industrial scale [23].

In general, the optimization of chemical reagents use is an important issue for the industrial application of Fenton processes due to its related high economical cost. A higher COD removal was achieved when a higher ratio of $[H_2O_2]$ was used in relation to the initial COD value of the solution (Fig. 2) because as more hydrogen peroxide is available, the generation of hydroxyl radical is also higher; although an excessive amount of H_2O_2 may scavenge hydroxyl radicals reducing the efficiency of the treatment [18]. In fact, this ratio between the used H_2O_2 concentration and the initial value of the COD in the solution was addressed to show the highest influence on the reduction of the COD (Fig. 3). As a consequence, COD removal losses derived from not performing the process under such a low optimum pH value did not result so important when the optimum amount of H_2O_2 is added to the solution (Fig. 2). In addition, the molar rate between reagents ($[H_2O_2]_0/[Fe^{2+}]_0$) resulted the second most important parameter influencing process efficiency. Its associated negative coefficient in the resulting RSM model (Table 1) implies that COD removal was enhanced when this ratio between reagents was lower. Therefore, considering certain amount of H_2O_2 is added to perform treatment, the higher tested related supply of Fe^{2+} yielded the higher removal of COD.

Table 1
Estimated regression coefficients and standard errors for quadratic model used in RSM analysis.

	Coefficient	Standard error
Constant	39.509	3.851
pH (X_1)	−5.489	1.671
$[H_2O_2]_0/COD_0$ (X_2)	11.503	1.656
$[H_2O_2]_0/[Fe^{2+}]_0$ (X_3)	−6.046	1.669
X_1^2	4.000	2.866
X_2^2	−2.625	3.283
X_3^2	−4.550	2.908
$X_1 \cdot X_2$	−2.679	1.990
$X_2 \cdot X_3$	0.083	1.986
$X_1 \cdot X_3$	3.836	2.022

In summary, the best tested reaction conditions achieved a 65% COD removal (pH = 2.8, $[H_2O_2]_0/COD_0$ = 4.250 and $[H_2O_2]_0/[Fe^{2+}]_0$ = 1). The COD remaining in the solution after this optimum treatment was characterized by the high content of volatile fatty acids (72.5 mg L^{-1}), which represents a high increase of biodegradability in the final solution. Therefore, the oxidative degradation of 1,4-dioxane at least resulted in the final persistence of more biodegradable organic acids, which is in agreement with previous results reporting an almost total destruction of 1,4-dioxane and a progressive decrease of the pH of the solution due to the formation of organic acids [1]. In addition, a poor elimination of the DOC further supported the degradation of 1,4-dioxane into more biodegradable products rather than to CO_2, which is also in agreement with previous related results [11].

In addition, more feasible industrial treatment conditions were chosen to perform further trials exploring the potential biodegradability enhancement of wastewater containing dioxane, namely: pH = 2.8, $[H_2O_2]_0/COD_0$ = 2.125 and $[H_2O_2]_0/[Fe^{2+}]_0$ = 5. Higher doses of the reagents involve a proportional increase in the costs of chemicals and disposing iron sludge. Therefore, optimum reaction values resulting from RSM modeling are not really justified for real applications. As a result, a 43% COD removal was achieved performing the Fenton treatment of 1,4-dioxane under these reaction conditions; as well as the final presence of volatile fatty acids reached 58 mg L^{-1}, which also means a significant increase of the biodegradability of the final solution.

3.2. On-line FTIR monitoring of the degradation of 1,4-dioxane by Fenton oxidation

Concentration profiles of the main compounds that were generated in the solution along the Fenton oxidation of 1,4-dioxane (Fig. 4) were obtained monitoring the process with an on-line FTIR probe. The ConcIRT software identified the compounds that were being on-line detected by FTIR comparing them to the previously obtained reference FTIR spectra of these compounds (Fig. 1). Initially, FTIR spectra did not show any change after the addition of a low concentration of H_2SO_4 at the studied wavenumber spectral region; as well as it was shown that the degradation of 1,4-dioxane into ethylene glycol under acid reaction conditions resulted too slow to be detected at the beginning of the reaction (Fig. 5). In fact,

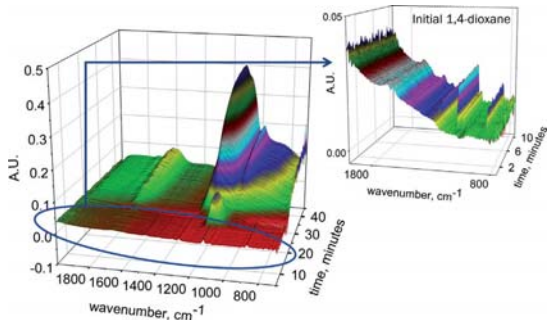


Fig. 4. Evolution of FTIR spectra within the 2000–750 cm^{-1} region along the Fenton treatment of 1,4-dioxane. *Reaction conditions*: [1,4-dioxane] = 70 mmol, pH = 2.8 ± 0.2, $[H_2O_2]_0/[Fe^{2+}]_0$ = 5.

the absence of ethylene glycol at this point was also checked by chromatographic analysis before the addition of Fenton's reagent, after which certain very early changes can be noticed in the spectra. The dissolution of ferrous sulphate heptahydrate reported a peak at about 1100 cm^{-1}, which surely represents sulphate ion [29]. The evolution of iron content cannot be followed separately.

1,4-Dioxane and $FeSO_4{\cdot}7H_2O$ were already present in the solution before any H_2O_2 was added. A red-brown color appeared just after hydrogen peroxide was incorporated, denoting iron oxidation from pale-green ferrous ion to red–orange ferric one. A final intense orange color remained in the solution during almost all the process. When 8.8 mmol of H_2O_2 were already added to the reaction medium, ethylene glycol began to increase its presence, as well as glycolic acid and oxalate anion; whereas 1,4-dioxane began to decrease (Fig. 5). After 35 mmol of H_2O_2 were fully added, glycolic acid and oxalate anion reached a maximum of absorbance and began to decrease their presence thereafter. On the other hand, the presence of formic acid was newly detected at this point, and increased much its content until reaching a constant value at the end of the reaction. Thereafter, the reaction evolved until the complete reduction of 1,4-dioxane just when all the H_2O_2 dosage (70.5 mmol) was added. In addition, the profile of ethylene glycol showed a slightly decreasing tendency at the same time that glycolic acid and oxalate anion increased their presence at a similar linear pace, denoting certain relationship between both trends toward the end of the process.

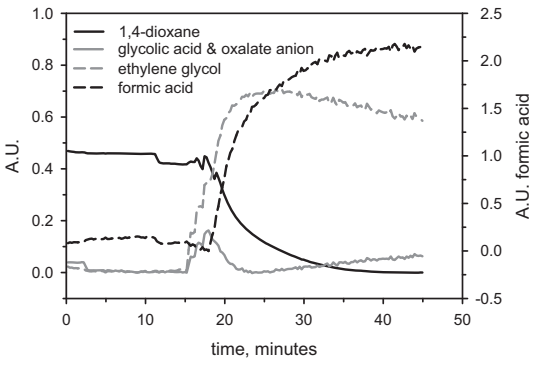


Fig. 5. FTIR-absorbance profiles of the main identified by-products that are produced during the Fenton oxidation of 1,4-dioxane. *Reaction conditions*: [1,4-dioxane] = 70 mmol, pH = 2.8 ± 0.2, $[H_2O_2]_0/[Fe^{2+}]_0$ = 5.

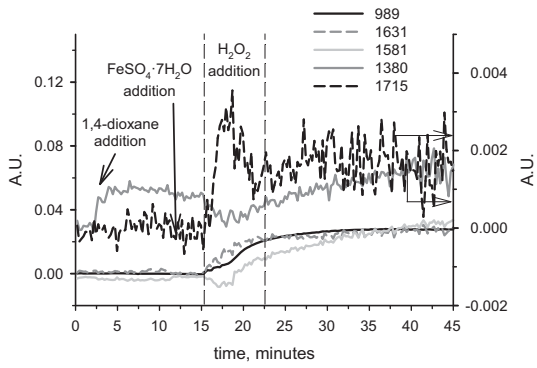
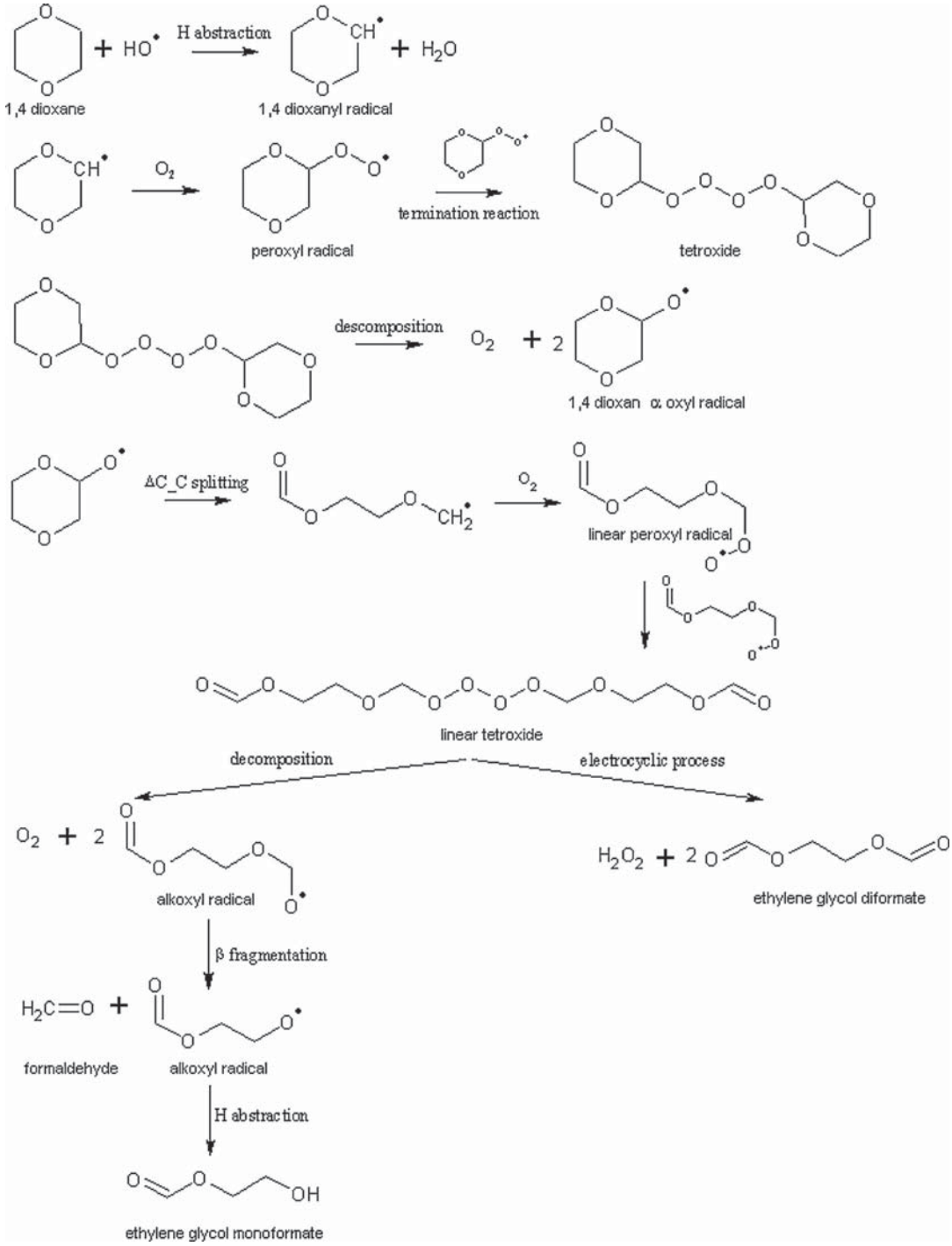


Fig. 6. FTIR-absorbance profiles representing the evolution of representative peaks along the degradation of 1,4-dioxane by Fenton's reagent within the spectral region of 2000–750 cm^{-1} (989 cm^{-1}: ethylene glycol and methoxyacetic acid; 1631 cm^{-1}: glycolic acid, oxalate anion, and oxalic acid; 1581 cm^{-1}: oxalate anion; 1380 cm^{-1}: 1,4-dioxane, ethylene glycol diformate, and formic acid; 1715 cm^{-1}: ethylene glycol diformate, methoxyacetic acid, and formic acid). *Reaction conditions*: [1,4-dioxane] = 70 mmol, pH = 2.8 ± 0.2, $[H_2O_2]_0/[Fe^{2+}]_0$ = 5.

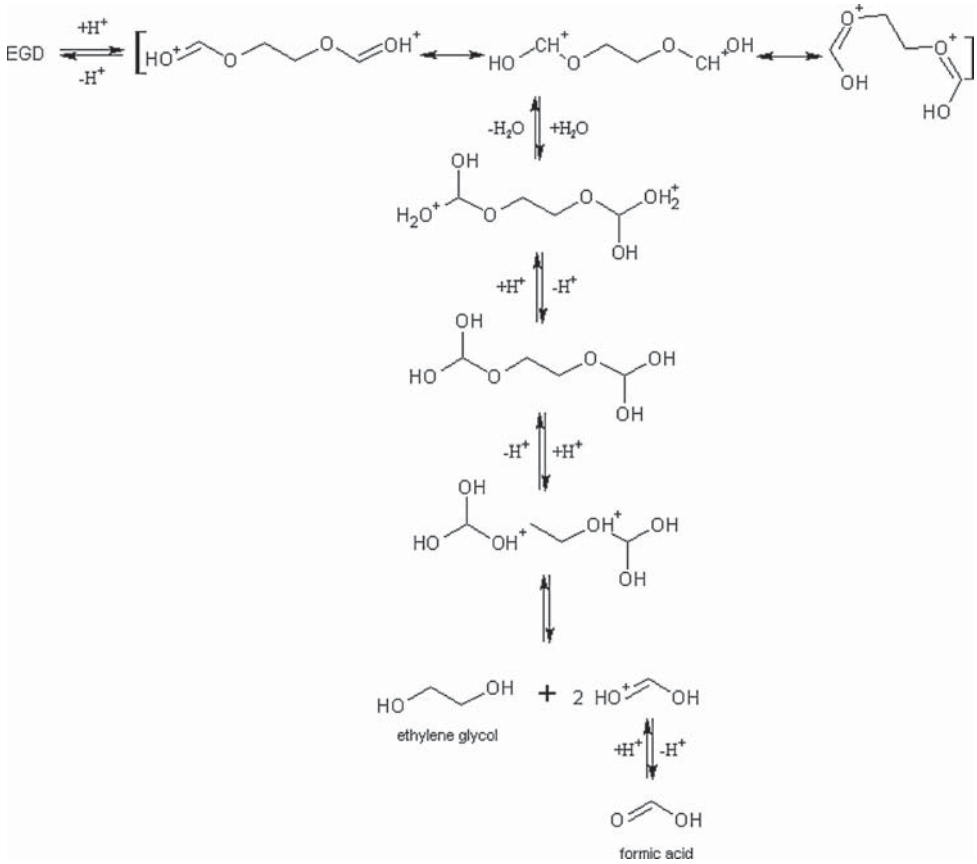
Chromatographic analyses confirmed the presence of all these compounds at the same moments of the reaction and the full removal of 1,4-dioxane at the end of the Fenton treatment. Therefore, the same process evolution shown in Fig. 5 was confirmed by the performed chromatographic determinations at singular reaction moments. Particularly, IC analyses indicated that, whether glycolic acid was produced in a small quantity, the presence of oxalate was very high. This might have been the result of a fast degradation of glycolic acid into oxalic acid, which may actually be the main responsible of the detected trend.

The pH-dependence of oxalic acid caused the appearance of the corresponding oxalate anion [30]. Some other peaks appeared along the reaction indicating the presence of other possible intermediates that the ConcIRT software could not identify, such as ethylene glycol diformate and methoxyacetic acid (Fig. 6). Complementarily, the chromatographic analyses detected the production of a low concentration of methoxyacetic acid and a negligible amount of acetic acid; whereas ethylene glycol was actually found along the reaction, which pointed out that the pathway of degradation mainly progressed through the formation of ethylene glycol diformate.

As a consequence, a mechanism for the degradation pathway that was followed along the Fenton treatment of 1,4-dioxane may be proposed based on a radical reaction mechanism (Schemes 1–3). First, hydroxyl radicals that were generated by the reaction between Fe^{+2} and H_2O_2, attacked 1,4-dioxane molecules to form 1,4-dioxanyl radical. Thereafter, this reaction proceeded until 1,4-dioxan-α-oxyl radical was obtained by the reaction of 1,4-dioxanyl radical with available dissolved oxygen (Scheme 1), first resulting in the formation of the peroxyl radical that next underwent termination reactions to generate the tetroxide precursor of 1,4-dioxan-α-oxyl radical, which was finally produced releasing oxygen [2,3,13]. Thereafter, 1,4-dioxan-α-oxyl radical progressed splitting the C–C bond, which was stabilized by ring opening. This linear peroxyl radical evolved then reacting with oxygen to produce a linear tetroxide that may undergo two further reactions: (1) the electrocyclic process of this linear tetroxide, which finally yields ethylene glycol diformate [2,13]; or (2) the decomposition in two alkoxyl radicals and oxygen, followed by β-fragmentation and H abstraction, finally producing ethylene glycol monoformate [13] (Scheme 1).

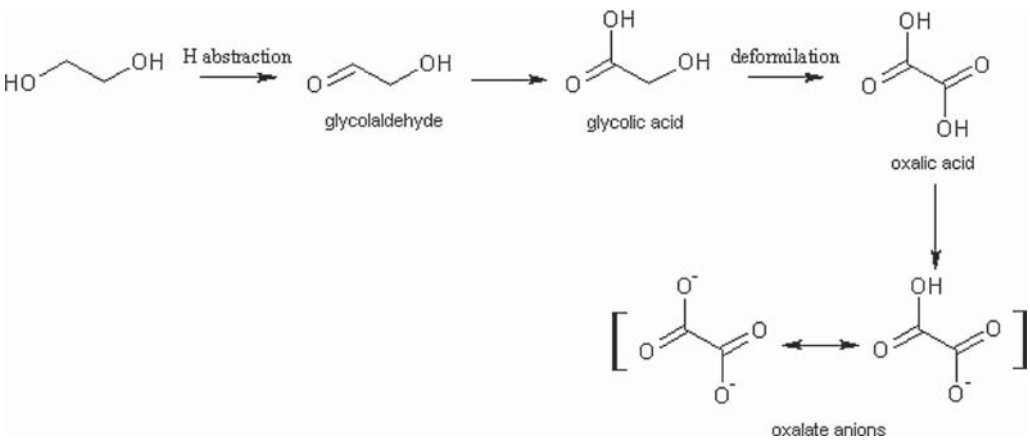


Scheme 1. Degradation mechanism generating ethylene glycol mono- and diformate from 1,4-dioxane.



Scheme 2. Degradation route for the acidic hydrolysis of ethylene glycol diformate into ethylene glycol and formic acid.

Stefan and Bolton [13] also proposed an alternative degradation pathway from 1,4-dioxan-α-oxyl radical consisting on the formation of methoxyacetic acid, and finally resulting in the formation of acetic acid. Although some peaks that were recorded along the reaction could be assigned to methoxyacetic acid (Fig. 6), and chromatographic analyses showed this by-product was somewhat produced, the almost completely absence of acetic acid along the reaction actually denotes that this degradation alternative was not significantly followed in comparison to the degradation pathway through ethylene glycol. Nevertheless, Beckett and Hua [2]



Scheme 3. Degradation route producing glycolic and oxalic acid from ethylene glycol.

reported that the degradation of methoxyacetic acid may also result in the generation of glycolic acid and formic acid.

Finally, ethylene glycol mono- and diformate may have progressed by acid hydrolysis to yield ethylene glycol and formic acid as by-products [31] (Scheme 2). Whereas ethylene glycol may be degraded to glycolic acid, and then evolve to oxalic acid by deformilation [32]; oxalic acid itself really shows up as oxalate anion under the acidic pH values predominating in the solution (Scheme 3).

In summary, during the oxidation of 1,4-dioxane, several by-products were produced as the consequence of the ring opening of 1,4-dioxane molecules, namely: ethylene glycol, glycolic acid, oxalate anion and formic acid. As a result, all 1,4-dioxane was removed, resulting in the appearance of more biodegradable by-products, which may allow a further biological treatment stage when necessary. An 80% total COD removal was finally achieved during these trials thanks to the previously identified optimum reaction conditions for this treatment and the further selection of a continuous addition mode for H_2O_2 during the process, which has previously been reported to address a similar treatment efficiency enhancement [18,19].

4. Conclusions

The treatment of 1,4 dioxane by Fenton's reagent achieved the total removal of this compound from wastewater, as well as 80% COD reduction efficiency under the best tested treatment conditions. In addition, wastewater biodegradability may be further enhanced, which has been addressed by a significant high presence of volatile fatty acids at the end of the reaction. Therefore, although the total mineralization of 1,4-dioxane was not achieved, final persisting by-products were highly biodegradable; thus allowing further conventional treatment if final disposal requirements make it necessary.

FTIR technique allowed the identification of the main compounds involved in the degradation of 1,4-dioxane by conventional Fenton treatment, as well as the control of the behavior of the target compound, denoting its presence and evolution along the reaction. This methodology also allowed addressing a new degradation mechanism, monitoring the formation of by-products, and optimizing the process identifying the presence of biodegradable compounds that may easily be treated by conventional biological technologies, which may furthermore represent a saving in the overall treatment cost.

Acknowledgements

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